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OF THE USSR

(ZHURNAL ANALITICHESKOI KHIMII)

IN ENGLISH TRANSLATION

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JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

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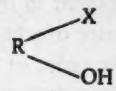
THE COLOR OF INTERCOMPLEX AND CYCLIC SALTS

A. A. Nemodruk

The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Acad. Sci. USSR, Moscow

The theoretical bases of photometric analysis and the mechanism of color reactions have still not been studied sufficiently [1, 2]. Despite the fact that in recent years, mainly thanks to the work of Soviet scientists (A. K. Babko, L. M. Kul'berg, V. I. Kuznetsov, I. M. Korenman, and N. P. Komar'), many important contributions have been made to the understanding of the mechanism of color reactions, to the choice of the optimum conditions for carrying them out, to making new highly sensitive organic reagents, and to studying the composition of colored complexes in solution, the question of clarifying the theory of organic reagents still remains untouched. Thus, up to now, these is still no unanimous view on the relation between the color of complex compounds in solution and their composition [3], while the physicochemical interpretation of color changes during complex formation with colored organic reagents is still to come. Recently, Kuznetsov proposed the so called hypothesis of intermolecular dissociation [3-7] for this purpose; unfortunately, this hypothesis does not have sufficient theoretical backing and contradicts many known facts.

According to this hypothesis the change in color which occurs during formation of a cyclic salt between a metal cation, which does not possess an intrinsic color, and a colored organic reagent of the type 

(where X=−OH, −COOH, = CO, = O, etc.), can be explained by intermolecular dissociation of one of the bonds formed between the element and the reagent , as a consequence of which the color of the latter approximates to the color inherent in the usual ionic state of the reagent. This approximation of the color of the complex to that of the reagent in its usual ionic state occurs in alkaline solutions, the approximation being the closer the more fully intercomplex dissociation is manifested .

On this basis the assumption was made that the extent of intermolecular dissociation of a complex cyclic salt formed by a metal ion not possessing a chromophoric action, with a colored reagent, can be quantitatively evaluated by choosing the appropriate concentrations of the undissociated and dissociated forms of the reagent so that their sum reproduces the color of the complex cyclic salt both with respect to shade and intensity [5].

Nevertheless, during a study of color reactions connected with the formation of cyclic salts , we established a number of facts which are incompatible with the hypothesis of intermolecular dissociation. A discussion of these facts , and their explanation from the point of view of modern polarization theory regarding the nature of the chemical bond, form the major content of the present article.

Comparative Study of the Light-Absorption Curves of Solutions of Reagents and their Complex Cyclic Salts

A study of the light-absorption curves of solutions of cyclic salts showed that they differ strongly from the light-absorption curves of solutions of reagents, the color of which coincides visually with the color of the solutions of the complexes. This coincidence of colors can be achieved in two ways.

An alkaline solution of the reagent is placed in one cell with a layer thickness of 10mm, while an acid solution of the reagent is placed in another cell. The total concentration of the reagent in both cells is a constant.

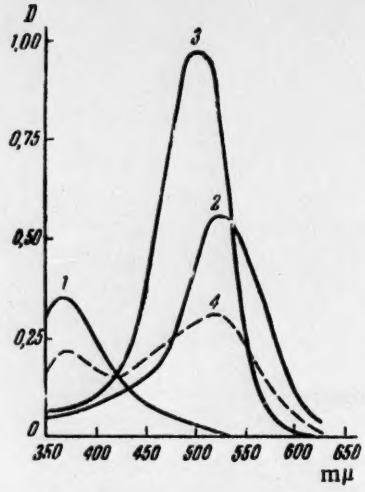


Fig. 1. Absorption curves for solutions of 3,4-dihydroxyazobenzene-4'-sulfonic acid and its cyclic zirconium salt. SF-4 spectrophotometer; cell with layer thickness 10 mm; reference solution, water. In all cases the reagent concentration was 7.4 mg/liter. 1) Reagent in 0.05 N HCl; 2) reagent in 0.05 N NaOH; 3) cyclic zirconium salt (Zr was taken in a 2.5-fold molar ratio to the reagent in order to exclude dissociation of the complex formed); reagent in 5% Na_2CO_3 solution, the color of which coincided visually with the color of the solution of the cyclic zirconium salt.

The concentrations of the alkaline and acid solutions are chosen so that on examining both cells placed one behind the other, the color coincides visually with the color of a solution of complex placed in the same cell; behind this is placed still one more cell filled with water.

The same effect can be produced by choosing the pH of the reagent solution so that its color coincides with the color of the solution of the complex.

It was found even in those few instances when it was possible to match visually the color of the solution of the complex with the total combined color of the undissociated and dissociated forms of the reagent that the nature of the light-absorption curves of such mixtures in the given instance, indicate two colored substances in solution, while the solutions of the complexes are characterized by light-absorption curves which are typical for a solution of one colored material.

As an example there is given in Fig. 1 the absorption curves for a solution of the complex of zirconium with 3,4-dihydroxyazobenzene 4'-sulfonic acid, and for solutions of the reagent itself in acid and alkaline media, as well as for a solution of the reagent, where the color of the solution matches a solution of the zirconium complex.

Similar results were also obtained with other cyclic salts of 3,4-dihydroxyazobenzene-4'-sulfonic acid, in particular, with the aluminum, gallium, germanium, and beryllium salts.

Other reagents behave in the same way, e. g. alizarin S (Fig. 2), 2,4-disulfobenzaurine-3',3''-dicarboxylic acid (Fig. 3).

Thus, by comparing the light-absorption curves of solutions of the complexes and of solutions of the reagents which match in color, it follows that in the case of solutions of reagents containing dissociated and undissociated forms of the reagents, each of these forms is independently reflected in the light-absorption curves, while in the case of solutions of the complexes, the dissociated and undissociated forms of the reagent are absent (under conditions where the reagent is completely bound as the complex, this being achieved by adding sufficient excess of the element). Instead of them there appears a new form which is intermediate between the dissociated and undissociated forms.

Levin [8] while studying the absorption spectra of cyclic complex compounds formed between ketoesters and multivalent metals, also found that in solutions of these cyclic complexes, the enol and ionic forms are absent. According to the light-absorption curves, these complexes occupy an intermediate position between the undissociated enols and their ionic state.

The absence of both the ionic form and the undissociated form of the reagent in solutions of the complex cyclic salts, is incompatible with the ideas regarding intermolecular dissociation of these salts developed by Kuznetsov [4,5].

The Color of Cyclic Salts in Solution and in the Solid State

The colors of cyclic salts in solution and in the solid state, as a rule, coincide quite well each other. At the same time the colors of the free reagents and their cyclic salts strongly differ from each other, independently of the form they are compared in. In Table 1 are given the colors of a number of known organic reagents and their cyclic salts both in solution and in the solid state. In those cases where in the solid state the deep tone of the color (blue, green) and its exceptionally high intensity complicate its determination, the dry preparations were ground with 50-200 times their amount of NaCl.

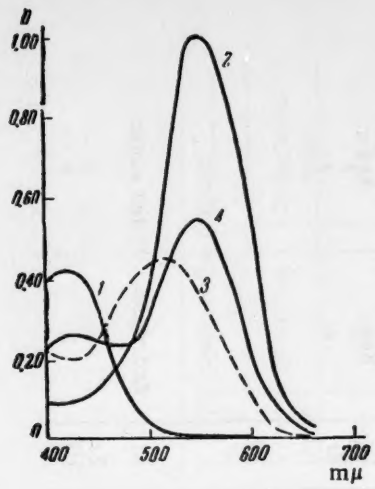


Fig. 2. Absorption curves for solutions of alizarin S and its cyclic zirconium salt. SF-4 spectrophotometer; cell with layer thickness 10 mm; reference solution, water. In all cases the reagent concentration was 18 mg/liter. 1) Reagent in 0.05 N HCl; 2) reagent in 0.05 N NaOH; 3) cyclic zirconium salt (Zr was taken in a 2.5-fold molar ratio to the reagent to exclude dissociation of the complex formed); 4) reagent solution, whose color matches visually the color of a solution of the cyclic zirconium salt.

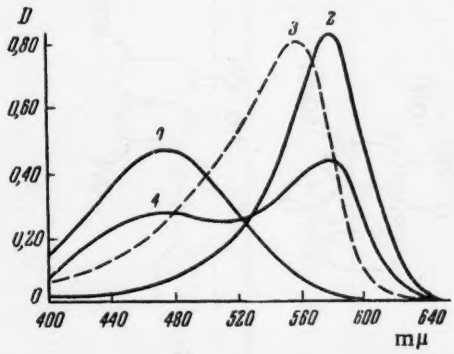


Fig. 3. Absorption curves for solutions of 2,4-disulfobenzaurine-3',3''-dicarboxylic acid and its cyclic zirconium salt. SF-4 spectrophotometer; cell with layer thickness 10 mm; reference solution, water. Reagent concentration in all cases 25 mg/liter. 1) Reagent in 0.05 N HCl; 2) reagent in 0.05 N NaOH; 3) cyclic zirconium salt (Zr was taken in a 2.5 fold molar ratio to the reagent for excluding dissociation of the complex formed); 4) reagent solution whose color matches visually the color of a solution of the cyclic zirconium salt.

As additional evidence to that given in Table 1 it should be pointed out that numerous metal-containing dyes (palatins, cibalans, neolans) which are soluble complex compounds of dyes with metals, color fabrics the same color that they exhibit in solution. Metal-containing dyes both in the solid state, on fibers, and in solution have the same colors. It should also be added that many color spot reactions on paper, and also developed paper chromatograms after drying, preserve their original color. Exceptions are so rare and insignificant, that the existence of such a regularity does not lead to any doubt.

The facts adduced are also incompatible with ideas regarding intermolecular dissociation, according to which the color of cyclic salts in solution should differ from their color in the solid state, in which, as is well known, neither ordinary nor intermolecular dissociation occurs.

Steric Hindrance

The very existence of cyclic salts, in which the metal ion is connected simultaneously with two functional groups directly by bonds having a definite length and direction in space, excludes the possibility of intermolecular dissociation. Even if one were to assume that, despite this obstacle, the ions were displaced in space, and in this way intermolecular dissociation were achieved, then, in this case, the cyclic salt containing the metal ion connected by only one functional group should not differ in any way from the ordinary noncyclic salt. However, the properties of cyclic salts show that they possess, in comparison with the corresponding noncyclic salt, exceptionally high stability. In this connection therefore the assumption of intermolecular dissociation of cyclic salts on the basis of one of two bands should be discarded.

Chemical Properties of Addenda in Complex Salts and in the Ionic State

It was pointed out recently in a number of papers [9-12] that there is an increase in the reactivity of certain organic compounds when in the form of their cyclic salts during azo coupling and nitrosation. According to the intermolecular dissociation hypothesis, this phenomenon would be explained by the presence of an intermolecular ionic state coinciding with the usual ionic state of the same organic compounds (chromotropic acid, pyrocatechol, salicylic acid) the amount of the ionic state being the same in both cases. However, in these papers it was established that there is a major difference between the chemical properties of organic compounds in the form of their cyclic salts, and in the usual ionic state. Thus, chromotropic acid, and in particular pyrocatechol, being in the ionic state in alkaline solutions, are readily oxidized by diazo compounds, as a result of which the corresponding azo compounds are either not formed completely or are formed in insignificant yields. In the case of cyclic salts the reverse is true; oxidation processes are suppressed giving way to azo coupling and nitrosation reactions.

TABLE 1

Colors of Some Organic Reagents and their Cyclic Salts in Solution and in the Solid State

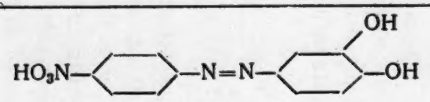
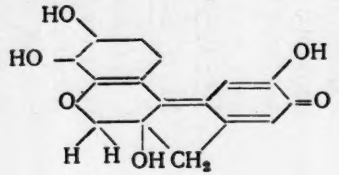
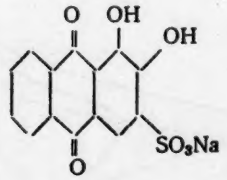
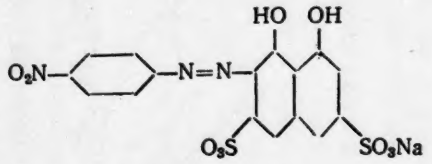
Reagent				Cyclic salt of the reagent		
		Color		With the element	Color	
Designation	Formula	In solution	In the solid state*		In solution	In the solid state*
3,4-Dihydroxyazobenzene-4'-sulfonic acid		Yellow	Yellow	Zr Hf Th	Red « «	Red » »
Hematein		Red	Red	Al	Blue	Blue
Alizarin red S		Yellow	Yellow	Pb Al Th Zr	Rose Red » »	Rose Red » »
Chromotrop 2B		Orange-red	Orange-red	Al Zr Hf	Red violet » »	Red violet » »

TABLE 1 (Continuation)

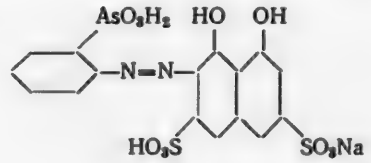
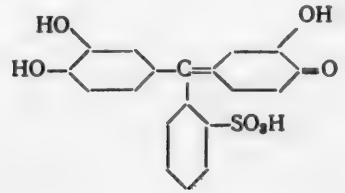
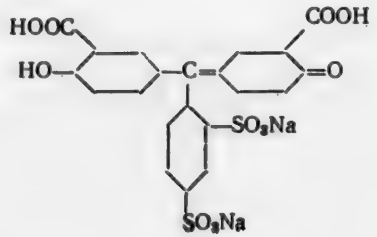
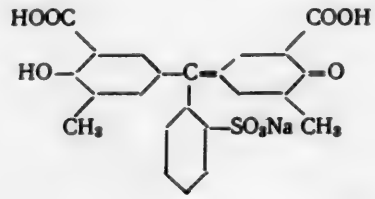
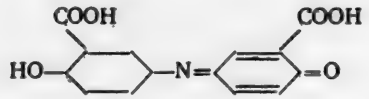
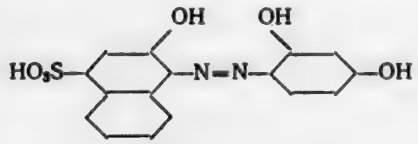
Reagent				Cyclic salt of the reagent		
		Color			Color	
Designation	Formula	In solution	In the solid state	With the element	In solution	In the solid state
Arsenazo		Red	Red	Be Al Th Zr	Rose » Blue-violet »	Rose » Blue-violet »
Pyrocatechol violet		Yellow	Yellow	Be Pb Zn Al Th Zr	Blue » » » » »	Blue » » » » »
2,4-Disulfobenzaurine-3',3''-dicarboxylic acid		Yellow-orange	Yellow-orange	Be Al Zr Th	Rose Violet » »	Rose Violet » »

TABLE 1 (Continuation)

Reagent				Cyclic salt of the reagent		
Designation	Formula	Color		with the element	Color	
		in solution	in the solid state		in solution	in the solid state
Eriochromcyanine		Orange	Orange	Al Zr	Violet »	Violet »
4-Phenolindophenol-3,3'-dicarboxylic acid		Red-orange	Red-orange	Be Zn Al Zr Th	Blue » » » »	Blue » » » »
2,4-Dihydroxybenzene-1-azo-1-2-hydroxynaphthalene-4-sulfonic acid		»	»	Zr Hf Th	Rose » »	Rose » »

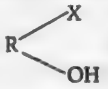
* The colors of the reagent in the solid state were determined after evaporating solutions to dryness. The pH of the evaporated solutions corresponded with the pH of the solutions of the cyclic salts the colors of which were compared.

This is explained by the fact that the electron pair on the phenolic oxygen atom in the cyclic salt, cannot switch over freely to the carbon atom as a result of its interaction with the neutral atom of the metal carrying a positive charge. The same is true for the suppression of decarboxylation during nitrosation of cyclic salts of salicylic acid [12]. If there actually were a similarity in the behavior of cyclic salts and alkaline solutions of the addenda themselves, there would be no need to use cyclic salts for facilitating syntheses which are difficult to carry out. Instead of cyclic salts, in the appropriate cases, it would be possible to use alkaline solutions of those same addenda, in which normal ionic state is manifested to the same extent as in cyclic salts.

Such a substitution is, however, out of the question. Thus, the calcium salt of chromotropic acid is readily coupled with 1-diazo-2-naphthol-4-sulfonic acid to give the corresponding azo compound, while under the same conditions, ordinary alkaline solutions of chromotropic acid at the same pH values, as a result of an increased tendency to oxidation, also react with the same 1-diazo-2-naphthol-4-sulfonic acid but without formation of the azo compound. [11].

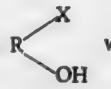
Thus, these differences which have been established between the chemical properties of addenda taken in the form of their cyclic salts, and of the same addenda in alkaline solutions, clearly contradict the hypothesis of intermolecular dissociation of cyclic salts.

Polarization Considerations

In accordance with modern ideas regarding the nature of the chemical bond [13-17], the ionic state of a reagent of the type  in an alkaline medium is the limiting case of the polarization of the O-H bond. In acid solutions such a reagent is found, as a rule, in a molecular form, in which the bond O-H is almost unpolarized. Replacement of the H atom by a metal which increases the polarity of the bond, leads to the appearance of a partial negative charge on the oxygen atom.

It is known that the changeover of colored organic compounds into an ionic state is accompanied by a change in their color [18]. It is true with the changeover of the colored organic material into an ionic state, the color does not change in those cases where the functional group — as the result of whose dissociation the material changes into the ionic state — is not conjugated with the chromophoric system of the colored material. If the bond in a molecule of a colored organic compound which can dissociate is polarized, then the color of such a compound will not coincide with the color of the same material either in the ionic or molecular form. Polarization of the bond to the same extent as the colored material approaches the ionic state, shows a corresponding effect on its color also [19].

Thus, Kul'berg [20] is of the opinion that if the polarity of the complex compound formed is greater than the polarity of the reagent itself, the depth of color will increase; while if the polarity of the compound formed is almost the same as the polarity of the reagent, then there will be hardly any change in color; and, if the new group depresses the polarity of the molecule then the color will be less intense.

Thus, the reason for the change in color of colored organic reagents of the type  which occurs during complex formation with metal cations not possessing an intrinsic chromophoric action, is not intermolecular dissociation of the cyclic salts, but the increase in polarity of the colored organic reagent.

Since dissociation into ions is the limit of the bond polarization, then in accordance with this, the change in color determined by the breakdown of the reagent into ions is always greater than the change in color which occurs during complex formation, as long as no additional changes occur in the structure of the reagent itself.

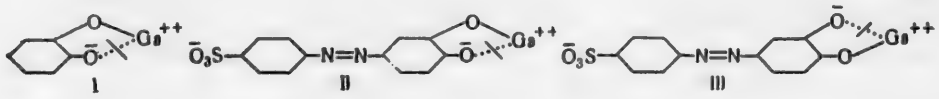
From the point of view of polarization considerations the similarity between the colors of cyclic salts in solution and in the solid state becomes understandable. The reason is that in both cases the bonds are polarized to the same extent.

Polarization considerations are also in good agreement with the nature of the absorption curves for solutions of cyclic salts, which indicate the absence of both dissociated and molecular forms of the reagent.

At the same time that intermolecular dissociation cannot be reconciled with the higher stability of cyclic salts as compared with the corresponding simple salts, from the point of view of bond polarization such an increase in stability would be necessary, since in this case the metal ion is connected with the reagent not by one but by two bonds simultaneously.

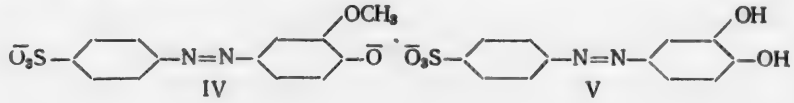
As indicated already, the hypothesis of intermolecular dissociation of cyclic salts presupposes dissociation along only one of the two bonds of the metal with reagent [4]. This assumption was made on the grounds that dissociation along two bonds simultaneously is incompatible with the existence of the cyclic salt itself [4]. Such a difference in the nature of the two bonds can be justified to some extent only in those cases where both the functional groups of the reagent forming the bond with the same metal ion are different. When these groups are completely identical, as for example in the cyclic gallium salt of pyrocatechol, the structure of which according to Kuznetsov [4] is that given in form I, then the assumption regarding the inequality of the two completely similar bonds contained in this cyclic salt, an assumption which Kuznetsov made without any proof, cannot be justified. The work of Calvin and Wilson [21] confirm that these bonds are of equal value.

Further, in choosing one of the two structures of the gallium complex (II or III), formed in weakly acid solution during the interaction

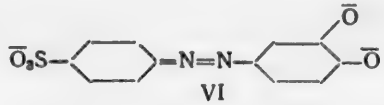


I II III

of 3,4-dihydroxyazobenzene-4-sulfonic acid with Ga^{3+} ions, Kuznetsov proceeds on the grounds that the color of solutions of the complex formed is closer to the color of the alkaline solutions of 3-methoxy-4-hydroxyazobenzene-4'-sulfonic acid (IV), and not of the acid (V) or alkaline (VI) solutions of 3,4-dihydroxyazobenzene-4'-sulfonic acid. Moreover, the dissociation of



IV V



VI

the hydroxyl group in position 3 has an insignificant effect on the color, this is taken as evidence against structure III. On this basis structure II was chosen.

However, solutions of the cyclic gallium salt of 3,4-dihydroxyazobenzene-4'-sulfonic acid proved to be deeper colored than solutions of IV. According to the intermolecular dissociation hypothesis solutions of the gallium cyclic salt should not have a deeper color than solutions of IV, even if there was complete intermolecular dissociation of one of the two bonds. Accordingly, the hypothesis of intermolecular dissociation is not confirmed in this case even by the example cited by V. I. Kuznetsov. This difference between the colors of solutions of the cyclic gallium salt (II) and of an alkaline solution of 3-methoxy-4-hydroxyazobenzene-4'-sulfonic acid (IV), which contradicts the hypothesis of intermolecular dissociation, can be explained on the grounds that in the cyclic gallium salt (II) there is a substituent OGa^{2+}, which gives rise to a somewhat deeper color than the substituent OCH_3 in compound (IV).

From the point of view of the polarization of the bonds there is no need in the case of the cyclic gallium salt of pyrocatechol (I) to make a compulsory distinction between the two similar bonds formed by the metal ion, in order to explain its enhanced chemical activity. In the given instance, these bonds are polarized to the same extent. In other cases they may be polarized to varying extents, as a consequence of inequalities in the functional groups which directly form the bonds with the metal ion. Recognition of the polarity of both bonds in the cyclic gallium salt formed during the interaction of 3,4-dihydroxyazobenzene-4'-sulfonic acid with Ga^{3+} ions, makes it easy to explain the somewhat more reddish shade of the color of solutions of the cyclic gallium salt in comparison with that of alkaline solutions of 3-methoxy-4-hydroxyazobenzene-4'-sulfonic acid (IV). In actual fact,

depending on the degree of polarization of both bonds of the reagent with Ga^{3+} ions, the color of a solution of the cyclic salt can be either darker or lighter than the color of an alkaline solution of 3-methoxy-4-hydroxyazobenzene-4'-sulfonic acid. From the point of view of bond polarization, the possible limits of the color changes of solutions of cyclic salts are extended: the colors of solutions of the cyclic salts may change (depending on the metal ion) from the color of the reagent itself in acid solutions to the color of its alkaline solutions.

TABLE 2

Colors of the Sodium and Potassium Salts of Nitrophenols [22]

	Sodium salts	Potassium salts
o-Nitrophenol	Intense yellow	Red
p-Nitrophenol	Almost colorless	Yellow

The hypothesis of intermolecular dissociation of cyclic salts cannot explain the change in color of reagents forming simple salts but not cyclic salts. Changes in color during formation of simple compounds is the result of bond polarization. From polarization considerations it is easy to explain the differences in color of a number of simple salts, e. g., the sodium and potassium salts of o- and p-nitrophenols (see Table 2). K^+ ions form bonds which are more polarized than those formed by Na^+ ions, as a result of which the potassium salts of o- and p-nitrophenols are more deeply colored than the corresponding sodium salts.

The coincidence of the red color of an alkaline solution phenolphthalein with the color of its solid salt [23] found in the undissociated form a coincidence which cannot be explained on the basis of the theory of ionic colors is readily explained by the fact that in the solid salt of phenolphthalein the bond with the metal is strongly polarized, as a result of which it approximates to the ionic state of phenolphthalein with respect to its effect on color.

On this basis of polarization considerations, it also becomes clear why the color which develops during the absorption of reagents of the type ROH on hydroxide precipitates and on the insoluble salts of a number of metals are similar to the colors of aqueous solutions of these reagents on addition of alkali. From this it follows that absorption is equivalent, to a certain extent, to the electrolytic dissociation of these reagents, when a proton splits off and a phenolate is formed. However, the maxima of the absorption bands of the absorbed phenols do not coincide accurately with those for the phenolate ions, and show a characteristic dependence on the electrostatic field on the surface of the crystal lattice. Thus, during the adsorption of p-nitrophenol, thymolphthalein, and alizarin on BaF_2, and CaF_2 the color change is stronger in the case of BaF_2 than CaF_2 [24].

The hypothesis of intermolecular dissociation of cyclic salts cannot explain the change in color of adsorbed reagents. Being fundamentally unsound it can only show a negative influence on the further development of the theoretical bases of photometric analysis. In view of this it should be replaced by polarization considerations which have received general recognition in modern chemistry.

As for the designation of polarization bonds, then in those cases where it is necessary, the symbols generally accepted at present should be used [13, 25, 26], i. e., the shift of an electron pair should be designated either by means of straight or curved arrows, or by the symbols for atoms marked with signs of incomplete (partial) charges.

SUMMARY

It has been shown that the hypothesis of intermolecular dissociation of cyclic salts which presupposes the dissociation of one of the two bonds of the cyclic salt with formation of an intermolecular ionic state, has no factual basis.

It has been found that the nature of the light absorption curves of solutions of cyclic salts, the coincidence of their color in solution and in the solid state, and the enhanced reactivity of the cyclic salts as compared with that of the free reagents under identical conditions, are all incompatible with the hypothesis of intermolecular dissociation of cyclic salts.

It has been shown that all the specific properties of cyclic salts can be satisfactorily explained on the basis of the polarization of the bonds formed between the organic reagent and the metal ion.

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SPECTROPHOMETRIC STUDIES OF REACTIONS WHICH ARE IMPORTANT IN ANALYTICAL CHEMISTRY

COMMUNICATION 2. COMPLEX COMPOUNDS FORMED BY COPPER IONS WITH SODIUM 2-NITROSO-1-NAPHTHOL-SULFONATE*

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The A.M. Gor'kii Kharkov State University

Substituted 1-nitroso-2-naphthol and 2-nitroso-1-naphthol are finding wide application in analytical chemistry, particularly in photometry. Thus, nitroso-R-salt (sodium 1-nitroso-2-naphthol-3,6-disulfonate) is used for the photometric determination of cobalt [1]. The same reagent has been proposed for determination of iron [2]. Another compound, sodium 2-nitroso-1 naphthol-4-sulfonate** , as Sarver [3] showed in 1938, also forms colored compounds with cobalt, iron, copper, and nickel. This reagent was again mentioned in a number of review articles [4-6]. Recently a paper appeared in which a method was described for the photometric determination of cobalt by means of this material [7]. It is clear from these papers that nitroso-N-salt like the nitroso-R-salt can be used for determining cobalt.

Earlier we studied the composition, optical properties, and stability of the compounds which nitroso-N-salt forms with cobalt [8] and nickel [9]. Cobalt is found in the trivalent state in the complex compounds formed with both nitroso-N-salt and nitroso-R-salt, and forms CoR_3 [10,11]. With nickel, two compounds NiR and NiR_3 are formed, although the possibility of the formation of an intermediate compound NiR_2 cannot be overlooked [9]. The present article contains results of a study of the complexes of copper with nitroso-N-salt.

Sodium 2-nitroso-1-naphthol-4-sulfonate was prepared according to Witt and Kaufman's procedure [12], and in addition was recrystallized twice from water and then washed with alcohol. The absorption curves of solutions with equal concentration of material, after the first and second recrystallization, coincided with each other exactly. Cupric sulfate was crystallized twice. The copper concentration of the solutions was determined iodometrically. The optical density was measured on a spectrodensograph [13], while the pH was controlled potentiometrically by means of a glass electrode. A definite pH value was established by means of HCl or NaOH, in order to avoid the necessity of taking into account the interaction of copper ions with the components of buffer mixtures.

In Fig. 1 are given the absorption curves for solutions of Cu^{2+} ions and nitroso-N-salt in the proportion of 1:3, at various pH values. The initial concentration of copper $C_{Cu_2^+} = 2.1 \times 10^{-4}$ M/liter. Curves 1 and 9 almost coincide with the absorption curves of nitroso-N-salt at the corresponding pH values. At pH 10, after removal of the precipitate, the absorption curve of the filtrate coincides exactly with the absorption curve of the nitroso-N-salt of the same concentration and at the same pH. This indicates complete breakdown of the complex compound. It is interesting to note that the analogous complex with nickel is completely stable under the same conditions [9]. As becomes clear later, this is not connected with the lesser stability of the copper complexes, but with the higher hydrolysis constant of the copper ions.

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* For Communication 1 see J. Anal. Chem. 9,151 (1954) [C.B. Translation].

** In order to shorten the name of this compound we shall henceforth call it "nitroso-N-salt" and designate it by the arbitrary sign RH.

Determination of the stoichiometric coefficients in the equation for the interaction of nitroso-N-salt with copper ions was carried out by the Ostromyslensky-Job method [14, 15, 16]. Experiments were carried out at pH 2, 3, 4, 5 and 6.5, 2-3 parallel determinations being made. Measurements were made at 540, 520, 500 and 480 mμ. In the first series the initial equimolar solutions had a concentration of copper and nitroso-N-salt of 1.2×10^{-3}, while in the second series the concentration was 3.0×10^{-3} M/liter. In Fig. 2 are given as an example typical "ΔD-mixture composition" curves. As is evident from the curves, the ratio of the stoichiometric coefficients at pH 2.0 and 3.1 is 1:1; while at pH 4.0 the maximum on the curve is diffuse and the ratio approximates to 1:2; at pH 5.0 and 6.5 the ratio is 1:3.

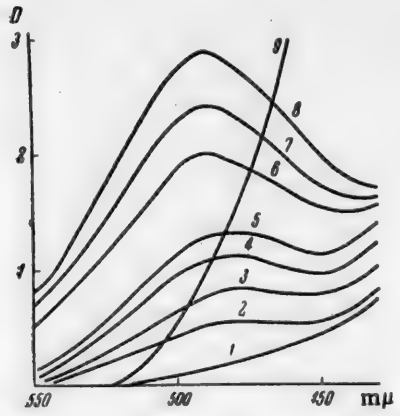

Fig. 1. Absorption curves for solutions containing 2.1×10^{-4} M/liter of Cu^{2+} ions and 6.3×10^{-4} M/liter of nitroso-N-salt, at various pH values: 1) pH 1.95 2) pH 2.50; 3) pH 3.00; 4) pH 3.50; 5) pH 3.95; 6) pH 5.00; 7) pH 6.10; 8) pH 7.30; 9) pH 10.

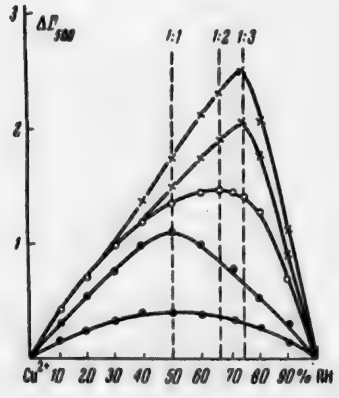

Fig. 2. Curves obtained by the Ostromyslensky-Job method; $C_{Cu^{2+}} = C_{RN} = 1.2 \cdot 10^{-3}$ M/liter; λ=500 mμ; l = 1 cm.
-●-●- at pH 2.0 and 3.1;
-○-○- at pH 4.0;
-×-×- at pH 5.0 and 6.5.

The following experiments were carried out in order to investigate the equilibrium in acid solutions at pH < 4. Under these conditions, apparently, one has to take into account the dissociation reaction based on the hydroxyl group of the nitroso-N-salt

$$RH \rightleftharpoons R^- + H^+, \quad (1)$$

the constant K_1 of which we determined earlier and was found to be 8.2×10^{-7} [17], and the reaction of the formation of the complex

$$Cu^{2+} + R^- \rightleftharpoons CuR^+ \quad (2)$$

with a constant K_2'.

The over-all reaction is expressed by the equation:

$$Cu^{2+} + RH \rightleftharpoons CuR^+ + H^+ \quad (3)$$

the equilibrium constant of which

$$K_I = K_1 \cdot K_2' = \frac{[CuR^+][H^+]}{[Cu^{2+}][RH]} \quad (4)$$

In order to calculate the molar extinction coefficients of the complex CuR^+ and the value of K_I, the optical density of solutions was measured in which $C_{Cu^{2+}} = C_{RH}$, $C_{Cu^{2+}}$ being varied within the limits $1.2 \times 10^{-3} - 3.0 \times 10^{-4}$ M/liter. Measurements were made at pH 2.15. Table I contains the results obtained for the optical density of the solutions at four wavelengths. The molar extinction coefficients were calculated on the basis of these results, using the formula suggested by Komar' [18]. For the case where the ratio of the stoichiometric coefficients in the reaction is equal to 1:1, the formula is of the form

$$\epsilon = \frac{1}{l} \cdot \frac{D_1 - nD_2}{C_1 - nC_2} \quad (5)$$

where D_1 and D_2 are the measured optical densities of solutions in which the copper ion concentrations are C_1 and C_2; l is the thickness of the layer in cm; $n = \sqrt{D_1/D_2}$. Using the values of C_1D_1 and C_2D_2 in pairs, we calculated the molar extinction coefficients for the four wavelengths: $\epsilon_{540} = 1050 \pm 180$; $\epsilon_{530} = 1850 \pm 270$; $\epsilon_{520} = 3030 \pm 320$ and $\epsilon_{510} = 3560 \pm 475$. The accuracy of the values of ϵ was established by the methods outlined in [19].

Knowing ϵ, and using the results given in Table 1, the authors calculated by means of the formula for Beer's law, the equilibrium concentrations of the complex, and then K_1. Results of these calculations are given in Table 1. $K_I = 7.5 \pm 0.5$. Since $K_I = K_1 \cdot K_2'$ and $K_1 = 8.2 \times 10^{-7}$, $K_2' = 9.2 \times 10^6$ and the instability constant of the complex $K_2 = 1.1 \times 10^{-7}$. As we see, the complex with copper is somewhat more stable than the corresponding complex with nickel, for which $K_2 = 1.3 \times 10^{-6}$ [9].

With increasing pH, complexes with a more complex composition appear in solution. As is evident from Fig. 2, at a pH of 4, formation of a complex CuR_2 is possible, although the maximum on the "ΔD -composition" curve is poorly defined. Careful examination of the absorption curves shown in Fig. 1 show that up to pH4, the maximum is located at 480 mμ, while at pH 5 and higher it is found at 490 mμ. All these facts indicate that if formation of an intermediate complex CuR_2 were possible, then its concentration should be very low. A similar state of affairs was observed for the nickel complexes. Assuming that in the given case also it is possible, to a first approximation, to neglect formation of a complex CuR_2, we studied the equilibrium at pH 6 and 7, where one might expect mainly formation of the complex CuR_3^- according to the reaction

$$CuR^+ + 2RH \rightleftharpoons CuR_3^- + 2H^+ \qquad (6)$$

for which

$$K = \frac{[CuR_3^-][H^+]^2}{[CuR^+][RH]^2} \qquad (7)$$

First, using the saturation method, we found the molar extinction coefficients for the complex CuR_3^-. For this mixtures were made up which contained excess nitroso-N-salt as compared with the copper ions, while the pH was adjusted to 7. Having measured the optical density of the solutions, and taking into account the intrinsic color of the nitroso-N-salt, the molar extinction coefficients were calculated by means of Beer's formula; these are given in the form of absorption curves in Fig. 3. At 540, 530 and 520 mμ they were found to be respectively: 4610, 6930, and 9500. Afterwards, measurements were made of the optical density of solutions with concentrations of $C_{Cu^{2+}} = 2.0 \times 10^{-4}$ and $C_{RH} = 6.0 \times 10^{-4}$ M/liter at pH 6.0 and 7.0 and at 540, 530, and 520 mμ.

Assuming that equilibrium (6) holds good, it is possible to write

$$D = \epsilon_{CuR}[CuR^+] + \epsilon_{CuR_3}[CuR_3^-] \qquad (8)$$

$$C_{Cu^{2+}} = [CuR^+] + [CuR_3^-] \qquad (9)$$

Simultaneous solution of these equations gives

$$[CuR_3^-] = \frac{D - \epsilon_{CuR} \cdot C_{Cu^{2+}}}{\epsilon_{CuR_3} - \epsilon_{CuR}} \qquad (10)$$

Calculating the value of $[CuR_3^-]$ by means of (10), it is then possible to find the remaining equilibrium concentrations, and, finally K. Table 2 contains the results of these calculations: $K = (5.2 \pm 2.6) \times 10^{-3}$.

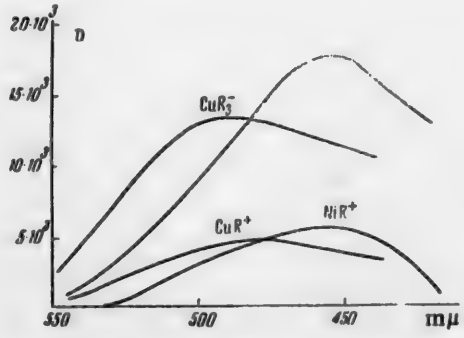

Fig. 3. Absorption curves for complexes of nitroso-N-salt with nickel and copper ions.

The sum of equations (3) and (6) gives

$$Cu^{2+} + 3RH \rightleftharpoons CuR_3^- + 3H^+ \qquad (11)$$

for which $K_{II} = K_I \cdot K = 3.9 \times 10^{-3}$. On the other hand, $K_{II} = K_1^3 K_3'$, where K_3' is the constant for formation of the complex according to the equation

$$Cu^{2+} + 3R^- \rightleftharpoons CuR_3^-. \qquad (12)$$

Consequently, the instability constant $K_3 = 1.4 \times 10^{-17}$. As we can see the complex CuR_3^-, just like CuR^+, is more stable then the corresponding nickel complex [9].

In conclusion, measurements were made of the optical densities of solutions in the pH range 2-5. The composition of the solutions was the same as in the previous experiments. If one disregards the formation of CuR_2, then in the pH range 2-5 we can confine ourselves to a consideration of the following equilibria:

$$Cu^{2+} + RH \rightleftharpoons CuR^+ + H^+ \qquad (3)$$

$$CuR^+ + 2RH \rightleftharpoons CuR_3^- + 2H^+ \qquad (6)$$

Here, $[Cu^{2+}]$, [RH], $[CuR^+]$, and $[CuR_3^-]$ are not known; while $[H^+] = h$, K_I and K, and also $C_{Cu^{2+}} = 2.0 \times 10^{-4}$ and $C_{RH} = 6.0 \times 10^{-4}$ M are known.

TABLE 1

Measured Optical Densities (D) of Solutions and Calculations of the Equilibrium Constant K_I: $C_{Cu} = C_{RH}$; pH = 2.15; l = 2 cm; $t^\circ = 20^\circ$

C_{Cu} Mol/liter	λ=540 mμ			λ=530 mμ			λ=520 mμ			λ=510 mμ		
	D	[CuR+]	K_I	D	[CuR+]	K_I	D	[CuR+]	K_I	D	[CuR+]	K_I
$1{,}2\cdot10^{-3}$	1,12	$5{,}3\cdot10^{-4}$	8,5	1,98	$5{,}3\cdot10^{-4}$	8,5	3,16	$5{,}2\cdot10^{-4}$	8,0	3.77	$5{,}3\cdot10^{-4}$	8,4
$1{,}0\cdot10^{-3}$	0,83	$3{,}9\cdot10^{-4}$	7,7	1,26	$3{,}4\cdot10^{-4}$	5,6	2,17	$3{,}6\cdot10^{-4}$	6,1	2,46	$3{,}5\cdot10^{-4}$	5,7
$6.0\cdot10^{-4}$	0,43	$2{,}1\cdot10^{-4}$	9,3	0,70	$1{,}9\cdot10^{-4}$	7,9	1,06	$1{,}7\cdot10^{-4}$	6,9	1,28	$1{,}8\cdot10^{-4}$	7.2
$4.0\cdot10^{-4}$	0,21	$1{,}0\cdot10^{-4}$	7,9	0,38	$1{,}0\cdot10^{-4}$	8,2	0,57	$9{,}4\cdot10^{-5}$	7,1	0,64	$9{,}4\cdot10^{-5}$	7,1
$3{,}0\cdot10^{-4}$	0,15	$7{,}1\cdot10^{-5}$	9,6	0,23	$6{,}2\cdot10^{-5}$	7,8	0,34	$5{,}6\cdot10^{-5}$	6,7	0,40	$5{,}6\cdot10^{-5}$	6,7

TABLE 2

Calculated Equilibrium Constant K $C_{Cu} = 2{,}0\times10^{-4}$ M/liter; $C_{RH} = 6{,}0\times10^{-4}$ M/liter; l = 1 cm

pH	λ=540 mμ				λ=530 mμ				λ=520mμ			
	D	[CuR_2^-]	[CuR+]	K	D	[CuR_2^-]	[CuR+]	K	D	[CuR_2^-]	[CuR+]	K
6,00	0,85	$1{,}80\cdot10^{-4}$	$2{,}0\cdot10^{-5}$	$5{,}6\cdot10^{-3}$	1,30	$1{,}83\cdot10^{-4}$	$1{,}7\cdot10^{-5}$	$9{,}4\cdot10^{-3}$	1,75	$1{,}76\cdot10^{-4}$	$2{,}4\cdot10^{-5}$	$3{,}2\cdot10^{-3}$
7,00	0,91	$1{,}96\cdot10^{-4}$	$4{,}0\cdot10^{-6}$	$7{,}7\cdot10^{-3}$	1,32	$1{,}95\cdot10^{-4}$	$5{,}0\cdot10^{-6}$	$3{,}9\cdot10^{-3}$	1,86	$1{,}93\cdot10^{-4}$	$7{,}0\cdot10^{-6}$	$1{,}4\cdot10^{-3}$

In a previous communication [9] we derived equation (17), by means of which a similar system of equilibria was calculated. In the given instance the equation has the form

$$\frac{KK_1}{h^3}[RH]^4 + \frac{K_1}{h}[RH]^3 + \left(1 + \frac{K_1 \cdot C_{Cu^{2+}}}{h} - \frac{K_1 \cdot C_{RH}}{h}\right)[RH] - C_{RH} = 0. \quad (13)$$

By means of this equation we determined [RH], and then $[CuR^+]$ and $[CuR_3^-]$ for each pH value, i. e., we determined the concentrations of the colored components of the equilibria at 540, 530, and 520 mμ. Knowing these concentrations and the molar extinction coefficients of complexes CuR^+ and CuR_3^-, the optical densities of the solution were calculated. Results of these calculations are given in Table 3. As is evident from this table, the measured

TABLE 3

Calculated Equilibrium Concentrations as Functions of the pH

pH	[RH]	$[Cu^{2+}]$	$[CuR^+]$	$[CuR_3^-]$	D_{540}		D_{530}		D_{520}	
					calc.	meas.	calc.	meas.	calc.	meas.
2,55	$4{,}8 \cdot 10^{-4}$	$8{,}7 \cdot 10^{-5}$	$1{,}1 \cdot 10^{-4}$	$1{,}5 \cdot 10^{-9}$	0,12	0,12	0,21	0,18	0,34	**0,27**
2,95	$4{,}5 \cdot 10^{-4}$	$5{,}0 \cdot 10^{-5}$	$1{,}5 \cdot 10^{-4}$	$1{,}1 \cdot 10^{-8}$	0,16	0,16	0,28	0,25	0,45	**0,43**
3,50	$4{,}2 \cdot 10^{-4}$	$1{,}8 \cdot 10^{-5}$	$1{,}8 \cdot 10^{-4}$	$1{,}4 \cdot 10^{-7}$	0,19	0,16	0,34	0,32	0,57	**0,60**
4,00	$3{,}8 \cdot 10^{-4}$	$6{,}4 \cdot 10^{-6}$	$1{,}8 \cdot 10^{-4}$	$1{,}2 \cdot 10^{-5}$	0,24	0,21	0,44	0,49	0,68	**0,72**
5,00	$1{,}5 \cdot 10^{-4}$	$9{,}3 \cdot 10^{-7}$	$1{,}0 \cdot 10^{-4}$	$9{,}7 \cdot 10^{-5}$	0,56	0,60	0,86	0,90	1,23	**1,25**

values of the optical density ($D_{measured}$) are in good agreement with the calculated values ($D_{calculated}$) at all the pH values. This indicates that only the complexes CuR^+ and CuR_3^- are really mainly found in solution, while if any CuR_2 is formed, its concentration lies within the limits of experimental error.

In Fig. 3 are shown the absorption curves for the complexes formed between nitroso-N-salt and nickel and copper. The complexes NiR_3^- and CuR_3^- are important from an analytical point of view, since their absorption curves differ to such an extent, that, presumably, it should be possible to carry out a spectrophotometric determination of copper and nickel ions when they are present together.

As noted above, the complex CuR_3^- is more stable than the complex NiR_3^-; this is in agreement with the well-known fact that copper complexes are more stable than nickel complexes [20]. As for the spectral characteristics, the results obtained do not agree with the assumption that the absorption curves for the more stable complexes (similar in structure) should be displaced to a greater extent towards the short-wave side than the absorption curves for the less stable complexes [21]. Apparently, there is no such simple relationship here. Difficulties arise in trying to explain the nature of complexes. The complex CuR^+, obviously, is of the intercomplex type of compound, in which all the valence of the copper is not saturated. As for the complex CuR_3^-, then taking into account the divalence of copper, this complex is best related to the acidocomplex type. As can be seen from the absorption curves (Fig. 3), the maximum on the absorption curve for the complex CuR^+ is insignificantly displaced towards the red side (by 10-15 mμ) on connecting another two molecules of RH to CuR^+. This indicates that the bond between these two molecules in the complex CuR_3^- is electrostatic in character. In this case the spectra have an approximately additive character. The small shift of the absorption toward the red side is caused by the intermolecular Stark effect as a result of the field of the connected molecules of the nitroso-N-salt distorting the system of terms of the CuR^+ complex [22].

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SUMMARY

It has been established that two complex ions, CuR^+ and CuR_3^-, are formed in solutions containing copper ions and sodium 2-nitroso-1-naphthol-4-sulfonate, depending on the pH of the solution. The molar extinction coefficients of these complexes have been calculated as well as their instability constants. The complexes with copper ions are more stable than the corresponding complexes with nickel ions.

The NiR_3^- and CuR_3^- complexes are fairly stable and have high molar extinction coefficients. The difference in their absorption curves is large enough to permit the spectrophotometric determination of copper and nickel ions when present together.

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PRECIPITATION CHROMATOGRAPHY ON PAPER AS A METHOD FOR DETERMINING THE RELATIVE SOLUBILITY OF SPARINGLY SOLUBLE COMPOUNDS

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Studies carried out in order to elucidate the effect of various factors on the development of the zones of precipitates of individual sparingly soluble compounds led to the conclusion that the final dimensions of the zone belonging to one precipitate or another on the washed chromatogram is determined by the following factors: 1) by the value of the solubility product of the sparingly soluble precipitate (linear relationship); 2) by the concentration of the original solution (linear relationship); 3) by the volume of the drop of test solution (linear relationship); 4) by the nature of the precipitate formed (formation of crystalline precipitates terminates on a narrower part).

All other conditions being equal, the zone width of any particular precipitate on a washed chromatogram depends exclusively on the value of the solubility product of the sparingly soluble compound.

The precipitate on the washed chromatogram occupies a smaller area, the lower the value of its solubility product, and consequently the lower its solubility. Obviously, it should therefore be possible to assess the relative solubility of various precipitates on the basis of the zone width of these precipitates on a washed chromatogram.

In order to obtain data on the comparative solubility of various precipitates, it is necessary to obtain washed precipitation chromatograms of the individual sparingly soluble compounds. The washed chromatograms must be developed. On the developed chromatograms it is then necessary to determine the zone dimensions of the corresponding precipitates, and the results obtained compared with each other. As a result it is possible to compile a series of precipitates in decreasing or increasing order of solubility. The least soluble precipitates form the zones with the smallest dimensions on the chromatogram.

Method and Experimental Technique

Reagent paper was prepared by soaking ordinary filter paper (OST 6717/58) with 1-4% aqueous solutions of the alkali metals which serve as the precipitant. Excess solution was allowed to drain, and the paper bands then dried in air in a hanging position.

The primary chromatogram was obtained by placing a drop of 0.1 N test solution by means of a capillary provided with a rubber bulb, on a band of reagent paper 65 x 65 mm. During this stage the drop was allowed to drop freely into the paper from a height not greater than 5 mm from the paper surface. After the drop had dispersed in the paper pores in a radial direction, the primary chromatogram was formed in the shape of a round spot.

The washed chromatogram was obtained by placing drops of distilled water in the center of the moist round spot in succession, in the same way as that adopted for obtaining the primary chromatogram. In order to get the final dimenssions of the zone it was necessary to superimpose five-six drops of water. Each new drop was placed on the paper only after the preceding drop had completely soaked in.

The washed chromatogram was also the developed chromatogram in those cases where the precipitate formed had its own intrinsic color. In those cases where precipitate was colored, it was developed by means of a reagent which reacts with it to give colored compound.

The chromatograms were developed by spraying the dry, washed chromatogram with a solution of developing reagent supplied from a sprayer. The developer was applied to the paper observing the following conditions: a) the solution was applied in a fine uniform spray; b) the solution was applied in several small portions; c) excessive soaking was avoided, a new portion only being applied after the former had been completely absorbed.

The zone of an individual sparingly soluble compound on the developed chromatogram was in the form of a colored round spot. In the case of two more precipitates applied simultaneously, the soluble precipitate formed the center in the form of a round spot, while the others formed colored rings surrounding the center spot. The precipitates follow one another from the center to the periphery in order of increasing solubility.

Test Materials and Experimental Results

The relative solubility of silicates, phosphates, arsenites, ferrocyanides, chromates, and several other sparingly soluble compounds was determined by precipitation chromatography on paper by the drop variant. In order to get the precipitation chromatograms, the paper was treated with the following solutions of the alkali metal salts respectively: 4% sodium silicate, 3.5% sodium hydrogen phosphate (disubstituted), 3.5% sodium arsenite, 1.0% potassium ferrocyanide, and 3% potassium chromate. The paper soaked with potassium ferrocyanide contained the equivalent amount of precipitant with respect to the test ions. Bearing in mind that complex formation proceeds stepwise, with formation of coordinately saturated and unsaturated compounds [1], and also of mixed compounds [2], other concentrations of the precipitant (0.5-5%) were tried in addition to those mentioned above. The content of other precipitants in the reagent paper was two-three times the equivalent amount of the test ions.

Calculation of the concentrations of the solutions to be used for treating the paper, so that the paper contained the equivalent amount of precipitant in the zone where formation of the given precipitate occurs, was based on the following. When a volume V (cm^3) of test solution in the form of drop flows along the pores of the paper, and its concentration is Co(mg-equivalent / cc) the absorption capacity of the precipitant should be given by:

$$A = Sh\gamma a,$$

where S is the in cm^2 area of the paper, on which the drops of test solution (cc) spread; h is the paper thickness in cm; γ is the density of the precipitant in the paper pores, in mg/cm^3; and α is the specific absorption capacity of the precipitant, in mg-equivalents/mg.

In accordance with the law of equivalents and with the law of conservation of matter, the following equation should hold:

$$Sh\gamma a = CoV. \qquad (1)$$

The product $Sh\gamma$ is the weight (g) of precipitant in the volume in which formation of precipitate occurs, while the reciprocal of the specific absorption capacity of the precipitant (1/a) is simply its equivalent weight (E). Taking this into account, relation (1) can be expressed as

$$g = CoV \cdot E. \qquad (2)$$

The weight of precipitant (g) corresponding to the volume of the drop of test solution is expressed in mg. In order to convert its concentration into grams per 100 ml of solution (G) the following formula is suitable:

$$G = Co \cdot E \cdot 100. \qquad (3)$$

The materials to be precipitated were used in the form of 0.1 N solutions of the nitrates of those cations which form sparingly soluble compounds with a given precipitant. The drop volume of the solutions prepared was measured with a microburet (the volume was 0.025 ml). In all experiments the concentrations of the solutions of the materials being precipitated, and also the volume of the drops were kept constant. Under these conditions, the difference in the dimensions of the zones of the precipitates obtained could only be attributed to the differences in the solubilities of the precipitates.

The developers used (Table 1) were organic reagents which formed with the precipitates on the washed chromatogram, even less soluble compounds with a bright characteristic color. The zone width of the precipitates of individual sparingly soluble compounds were measured on the developed chromatograms with an accuracy of 0.1 mm. The results obtained are given in Table 2.

When the precipitates differed from each other with respect to solubility, the zone dimensions of the separate precipitates on paper soaked with the same precipitant, differed from each other. From the relative dimensions of the zone of the precipitates studied, a scale was compiled of the comparative solubilities of these precipitates on the basis of the linear relationship between the width of the precipitate zone on the developed chromatogram and its solubility.

In order to fix the position of each member in a sorption series of solubility more accurately, the elements were taken in pairs. When the pair of cations taken separated in the form of precipitates, two zones were found on the developed chromatogram. The first zone, belonging to the least soluble of the two precipitates, was obtained in the form of a round spot with a characteristic color, in the center, at the point where the drop of test solution was placed on the paper. The zone of the more soluble precipitate was located on the periphery of the first zone in the form of a ring of a different color. Precipitates which were equally soluble appeared as a mixed zone on the developed chromatogram. In the sorption series of solubility such precipitates occupy the same position. The following series of precipitate solubilities were obtained (the series are in increasing order of solubility):

1. The series obtained on a paper soaked with sodium silicate

$$Hg^{2+}—Fe^{3+}—\underset{|}{Bi^{3+}}—Hg_2^{2+}—Al^{3+}—Cd^{2+}—Pb^{2+}—Cu^{2+}—Ag^{+}—Zn^{2+}—Mn^{2+}—\underset{|}{Co^{3+}}—\underset{|}{Ba^{2+}}$$
$$\qquad\qquad\qquad\qquad\quad Cr^{3+}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Ni^{2+}\qquad Sr^{2+}$$

2. The series obtained on paper soaked with sodium arsenite

$$Hg^{2+}—\underset{|}{Fe^{3+}}—Cr^{3+}—Bi^{3+}—Al^{3+}—Cu^{2+}—Pb^{2+}—Ag^{+}—Cd^{2+}—Zn^{3+}—\underset{|}{Co^{2+}}—Ba^{2+}—Sr^{2+}$$
$$\qquad\qquad\quad Hg_2^{2+}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Ni^{2+}$$

3. The series obtained on paper treated with sodium hydrogen phosphate (disubstituted)

$$Hg^{2+}—\underset{|}{Fe^{3+}}—Al^{3+}—Cr^{3+}—Bi^{3+}—Pb^{2+}—Cu^{2+}—Ag^{+}—\underset{|}{Cd^{2+}}—\underset{|}{Mn^{3+}}—Ni^{2+}—Sr^{2+}—Mg^{2+}$$
$$\qquad\qquad\quad Hg_2^{2+}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Zn^{2+}\quad Co^{2+}$$

4. The series obtained on paper soaked with potassium chromate

$$Hg_2^{2+}—Bi^{3+}—Hg^{2+}—Pb^{2+}—Ba^{2+}—Ag^{+}—Fe^{3+}—Al^{3+}—\underset{|}{Cd^{2+}}—Sr^{2+}—Co^{2+}—Ni^{2+}—Mn^{2+}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Zn^{2+}$$

5. The series obtained on paper soaked with potassium ferrocyanide

$$Ag^{+}—Cu^{2+}—Fe^{3+}—Zn^{2+}—\underset{|}{Ni^{2+}}—Bi^{3+}—Cd^{2+}—Pb^{2+}—Mn^{2+}—Al^{3+}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Co^{2+}$$

The solubility series obtained for the ferrocyanides differs from the series obtained previously [3].

The reason for the difference in the experimental results is that the composition and the properties (including solubility) of the ferrocyanides depend on the conditions used for preparing them. As indicated already [2], in addition to simple ferrocyanides of the type $Me_2^{2+}[Fe(CN)_6]$, there may also be formed mixed (binary and ternary) salts.

By a series of experiments it was established that the relative dimensions of the zones of the ferrocyanide precipitates of different metals, as well as their differentiation during separation of pairs of metals, depend significantly on the concentration of the precipitant in the paper. Copper and iron (III), cobalt and zinc, and

TABLE 1

Reagents-Developers

Developer	Concen., g/100 ml of solution	Solvent	Cations whose precipitate zones are developed
Alizarin —$C_{14}H_8O_4$	0,1	Alcohol	Al^{3+}, Fe^{3+}
Aluminon—$C_{22}H_{23}O_9N_3$	0,1	Distilled water	Al^{3+}, Cr^{3+}, Fe^{3+}
Benzidine-$C_{12}H_{12}N_2$	0,1	Acetic acid (50%-solution)	Mn^{2+}
Dithiozone-$C_{13}H_{12}N_4S$	0,05	Benzene	Zn^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}, Hg_2^{2+}, Hg^{2+}, Cu^{2+}, Ca^{2+}
Magneson—$C_{12}H_9O_4N_3$	0,025	Na OH (0,1 *N* solution)	Mg^{2+}
Sodium rhodizonate $C_6H_6Na_2$	0,1	Distilled water	Ba^{2+}, Sr^{2+}, Pb^{2+}
Rubeanic acid —$C_2H_4N_2S_2$	0,2	Alcohol	Ni^{2+}, Co^{2+}, Cu^{2+}

TABLE 2

Dimensions of the Zones of Various Precipitates (in mm)

Cations	Precipitates obtained on paper soaked with:					Cations	Precipitates obtained on paper soaked with:				
	Na_2SiO_3	Na_2HPO_4	Na_3AsO_3	$K_4[Fe(CN)_6]$	K_2CrO_4		Na_2SiO_3	Na_2HPO_4	Na_3AsO_3	$K_4[Fe(CN)_6]$	K_2CrO_4
Mg^{2+}	—	38,16	—	—	—	Co^{2+}	24,8	29,5	21,6	27,5	49,0
Sr^{2+}	25,8	36,0	27,2	—	42,5	Ag^{+}	21,5	27,5	16,3	14,5[31]	19,6
Ba^{2+}	25,7	29,3	25,0	—	22,2	Hg^{2+}_2	14,0	11,0	11,1	—	9,4
Al^{3+}	14,8	14,6	15.0	44,5	29,0	Pb^{2+}	16,8	18,0	16.1	30,5	17,4
Cr^{3+}	13,2	14,0	11,9	—	—	Hg^{2+}	7,8	8,0	9,6	—	11,2
Fe^{3+}	10,4	11,2	11,1	23,5	23,2	Bi^{3+}	13,2	17,6	12,7	28 5	10,0
Mn^{2+}	24,1	29,3	—	40,0	50,0	Cu^{2+}	20,0	22,5	15,6	22,0	36,1
Zn^{2+}	23,0	28.0	21,0	25,5	39,0	Cd^{2+}	16,0	28,0	20,0	30,0	39,0
Ni^{2+}	24,9	32,8	21,6	27,7	47,0						

also nickel and zinc, were not separated on paper soaked with 5% potassium ferrocyanide solution (excess precipitant), but were separated on paper soaked with 1% potassium ferrocyanide solution (an equivalent amount of precipitant). This could be a consequence of the formation of compounds differing in composition and solubility. Precipitates of copper, iron (III), bismuth, nickel, and cobalt, when excess precipitant is contained in the paper, separate out in the center (as a spot) and on the periphery (as a ring). When excess precipitant is used, presumably, there is obtained mixed (binary), appreciably soluble compounds which at the extreme position of the spot, after washing the primary chromatogram, are precipitated again.

Formation of two zones separated by a narrow ring of carrier (paper), was also observed in the case of silver precipitates when an equivalent amount of precipitate was contained in the paper. They were visible only at the moment of development (with dithizone). During separation of silver and copper in pairs these precipitates of silver which differ in properties and solubility were separated by the copper zone. It is an interesting fact with time these precipitates migrated; the more soluble silver zone migrated to the center, while the copper zone shifted towards the periphery of the spot.

Zinc and cadmium on separate chromatograms formed precipitates; the relative dimensions of zones indicated the possibility of separating these metals when taken in pairs. Nevertheless, when an attempt was made to separate these metals a mixed zone was obtained, this being presumably a consequence of the formation of binary and perhaps ternary salts.

It should be pointed out that the precipitates obtained on paper impregnated with other precipitants, sometimes differed in their composition from the composition of the corresponding salts. On paper impregnated with sodium silicate, iron ions (III) gave a precipitate of hydrated oxide with a cinnamon-brown color and not iron silicate, as a result of hydrolytic decomposition of the latter. On paper impregnated with sodium arsenite, cations of aluminum, chromium, and iron (III) formed hydroxide precipitates while bismuth gave precipitates of basic salts. The remaining cations gave arsenite precipitates. Hydroxide precipitates of aluminum, chromium, and i iron (III) (instead of phosphates) were formed on paper impregnated with sodium hydrophosphate. Bismuth separated out as the phosphate on the chromatogram.

The practical importance of a solubility series lies in the fact that they can furnish a basis for a possible separation of complex mixtures of materials. The members of any particular solubility series are more completely separated from one another, the further removed they are from each other in the series. Another criterion for completeness of separation of a mixture of materials in the form of precipitates, is the coefficient for the mean relative rate of movement of the precipitates K_b [3] which is defined by the equation

$$K_b = \frac{d_{M^+A^-}}{d_{K^+A^-}} = \frac{pL_{K^+A^-}}{pL_{M^+A^-}} \ldots (1)$$

where $d_{M^+A^-}$ and $d_{K^+A^-}$ are the diameters of the zones of the precipitates of the least soluble and most soluble compound, respectively, while $pL_{M^+A^-}$ and $pL_{K^+A^-}$ are the indices of the solubility products of these compounds.

It was established that a pair of inorganic ions can be completely separated in the form of precipitates on paper, when the value of K_b is equal to and less than 0.75. Partial separation of the precipitates of various metals is possible even for higher values of K_b, starting at a value of 0.95-0.96. Under these conditions, the smaller the value of K_b the more complete their separation. K_b can be said to be a quantitative measure of completeness of separation. K_b can be established merely by measuring the areas of the zones of the precipitates under consideration on the developed chromatograms and taking the ratio of the smaller area to the larger area. If it should prove to be less than 0.75, then complete separation of the precipitates should be possible.

Determination of the comparative solubility of precipitates by means of the method of precipitation chromatography on paper has not been studied in detail. The method enables one to get preliminary results to help in choosing the method of precipitation to be used for the separation of a complex mixture of materials.

SUMMARY

The possibility has been demonstrated of using precipitation chromatography on paper in a drop variant as a simple and rapid method of determining the relative solubility of sparingly soluble compounds. Sorption series for the comparative solubility of the silicates, arsenites, phosphates, chromates, and ferrocyanides of a large number of metals have been obtained.

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DETERMINATION OF THE ALKALI AND ALKALINE EARTH ELEMENTS IN SILICATE ROCKS BY MEANS OF FLAME SPECTROPHOTOMETRY

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Determination of the alkali and alkaline-earth elements in rocks is the most difficult operation in chemical analysis. For speeding up the determination of sodium and potassium in silicate rocks, Osborn [1] first used the method of flame photometry. Brannock and Berthold [2] used this method later for the analysis of minerals. The problem of the other alkali and alkaline-earth elements has been considered by other authors [3-9], but in each of these cases only one or two of the elements were considered, and only Horstman [10] determined rubidium, and cesium in the same solution. It is often necessary, however, for geochemical purposes, to determine the content of all the alkali and alkaline-earth elements in rocks and minerals simultaneously.

The work described in the present article is devoted to the development of a method for determining the alkali and alkaline-earth elements in granites, gneiss, syenites, microcline, and other silicate rocks and minerals. The spectrophotometer constructed is suitable for the determination of the alkali and alkaline-earth elements in an air-acetylene flame.

The optical system was a "DM" double-glass monochromator. The photoelectric setup includes a FÉU-17 photomultiplier (for the visible part of the spectrum) and a FÉU-22 photomultiplier (for the red and infrared part of the spectrum), a VVS-1 rectifier, and a M-21 mirror galvanometer with a sensitivity of 1×10^{-9} amp /mm. A spherical mirror 10 cm in diameter was set up behind the burner; this increased the sensitivity of the apparatus almost twice. The width for the inlet and outlet slits were chosen in the limits 0.05-0.08 mm for strontium and rubidium, while for sodium, potassium, lithium, and calcium this width was 0.08-0.12 mm. When lithium was determined in the presence of considerable amounts of strontium and calcium, the slit width was decreased to 0.05 mm and aluminum was added to the solution until its concentration was 1.5 mg/ml for decreasing the intensity of the strontium and calcium lines in the 670 mμ region. The indicated slit widths were the optimum values, since on increasing the slit width, the background increased more rapidly than the line intensity. By using a photomultiplier of a sufficiently high quality it was found possible to attain a sensitivity, in terms of γ/ml, of 0.005 with respect to lithium, 0.003 for sodium, 0.005 for potassium, 0.01 for rubidium, 0.05 for calcium, and 0.05 for strontium, when pure salts were used (for a deflection of the galvanometer through one division). Measurements of the emission intensity were carried out on the basis of the following lines: lithium 670.8, potassium 766.5, sodium 588.9, rubidium 780.0 or 794.7, calcium 549.8, strontium 460.7 mμ. The background was measured on both sides of the lines and the mean value taken.

During determination of group I and II elements, the test material was treated with hydrofluoric acid and perchloric acids. Other methods of decomposing test material were inapplicable; when sulfuric acid was used precipitates of the sulfates of the second group were formed, while on fusing test material with potassium or sodium carbonates, it is no longer possible to determine these elements.

A necessary condition for the determination of calcium and strontium is the absence of aluminum, which depresses the emission as a result of the formation of chemical compounds with high melting points.

TABLE 1

Activ. of the added Sr, impulses/min	Extraction with:	Activ. of the Sr extracted, impulses/min	Sr extracted, %
9380	H_2O	6715	71,4
9380	H_2O	8260	88,1
9380	2*N* HCl	9312	99,3
9380	2*N* HCl	9400	100

Removal of aluminum as the hydroxide can lead to adsorption of the alkali and alkaline-earth elements, so that reprecipitation is necessary. In order to avoid this we adopted Ahrens' method of concentrating the alkali and alkaline-earth elements [11], this consists in calcining the dry perchlorates and subsequently extracting the alkali and alkaline-earth elements with water. For this purpose we used 2 N HCl, completeness of extraction was controlled by using radioactive strontium Sr^{90}. The results obtained are given in Table 1.

EXPERIMENTAL PROCEDURE

An aliquot of carefully ground silicate (0.7-1.0 g) contained in a platinum basin is moistened with a few drops of water and 5-10 ml of perchloric acid and 15-20 ml of hydrofluoric acid added. The mixture is evaporated until the appearance of perchloric acid fumes. If the rock should not be completely decomposed after the first evaporation, the process is repeated with 5-10 ml of HF. For complete removal of fluoride after decomposition of the rock, the mixture is evaporated twice almost to dryness, a few drops of water and perchloric acid being added each time. The dry residue of perchlorates is then calcined at 500-550° for one hour. The perchlorates of the alkali metals are thereupon converted into the chlorides, while the alkaline-earth perchlorates are converted into the chlorides and partly into the oxides, and the perchlorates of the other elements into their oxides. The calcined residues are heated twice with 50 ml of 2 N hydrochloric acid, then twice with water, the solutions being collected each time in a beaker. During these operations only an insignificant part (5-7%) of the aluminum and iron oxides dissolve. Aluminum and iron are removed from the solution thus obtained by precipitation with ammonia (1:1) free from carbonate, the solution being neutralized to the methyl red endpoint. The precipitate is filtered off and washed; the solution is evaporated and then transferred to a 50 ml standard flask. For the determination of potassium and sodium, the content of which in rocks is rarely less than 1%, an aliquot of the solution is diluted so that the final concentration of potassium and sodium is within the range 5 to 50 γ/ml. The solution is always diluted when the content of the element to be determined is higher than the concentration at which there is observed a linear relation between concentration and emission. These concentrations, for which a linear relation is observed, were found to be up to 30 γ/ml. for lithium, up to 50-70 γ/ml for sodium, potassium, and rubidium, and up to 100-120 γ/ml for calcium and strontium.

The effect of various cations and anions on the emission of the alkali and alkaline-earth elements has been studied in detail in a number of paper [5, 12-14]. The choice of standards for test materials with an average content (more than 0.01%) of the alkali and alkaline-earth elements does not present any particular difficulty. For determination of lithium, rubidium, and strontium in granites, gneiss, and syenites, the standards contain potassium, sodium, calcium, and magnesium. To the standards for determining these elements, 1 ml of a solution containing 5% K_2O, 5.5% NaO, 0.5% CaO, and 0.5% MgO is added. For the analysis of rocks with a higher content of CaO and MgO, the amount of these elements added is increased to 2%. During determination of one of the three elements Na, K, and Ca, the standards used contain the other two elements in amounts equivalent to their content in the test rocks. Thus, for determination of potassium, the standards contain sodium and calcium. When the contents of the alkali and alkaline-earth elements is lower than 0.01%, the method of additions is used [15], in which the test solution is also the standard solution. For this purpose 4 aliquots of 10 ml each are taken from the original solution and transferred to 25-ml flasks. Water is added to one of these, while to the other three flasks are added accurate amounts of the solutions of the salts, so that the first of these flasks contains approximately the same amount of added salt as there is in the test material, while the second and third flasks contain twice, and four times the amount of added salt as there is in the first flask (see Table 2). The solutions obtained are then measured flame-photometrically, the background being measured on both sides of the lines. The background value is subtracted from the intensity of the line and the results plotted graphically (Fig. 1). The curve obtained is linear as long as the highest concentration of the salt does not exceed the values indicated above. The segment on the abscissa from the point of intersection of the straight line to the origin gives the content of the test elements in solution.

In order to check the method of additions, several experiments were carried out with synthetic mixtures to which various amounts of sodium, potassium, barium, and various acids were added. As the results in Table 3 show the error rarely exceeds limits of 5%. For low contents of several of the alkali and alkaline-earth elements

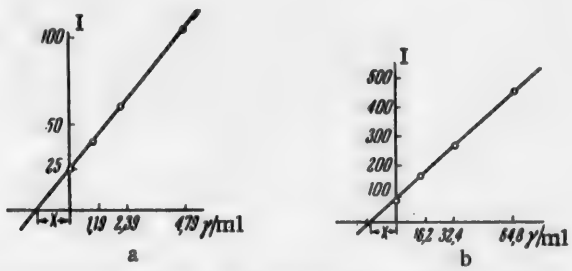
TABLE 2

Taken, γ/ml		Added, γ/ml						Found, γ/ml		Error	
		Flask 1		Flask 2		Flask 3					
Sr^{++}	Ca	Sr	Ca	Sr	Ca	Sr	Ca	Sr	Ca	Sr	Ca
1,33	15,6	1,19	16,2	2,39	32,4	4,79	64,8	1,36	15,4	+2,2	−1,3
26	82	48	171	68	266	113	449	Galvanometer deflection, background taken into account			

(of the order of 0.001%), the aliquot taken is increased to 1-1.5g, while 25% by volume of alcohol is added to the solution which is to be photometrically measured in order to decrease the depression of the line intensities of the alkali metals caused by the presence of a large excess of foreign salts.

The method was checked on international standard granite G-1 and diabase W-1. The results are given in Table 4.

During the determination of the alkali and alkaline-earth elements in several samples of granites, gneiss, syenites, microcline, and mica, the results given in Table 5 were obtained. The results obtained by the comparison method and by the method of additions are in good agreement with each other, and with those obtained by chemical and spectrographic methods.



Determination of the concentration of an element in solution by the method of additions: a) for Sr; b) for Ca.

TABLE 5

Rock	Method of determination	Li, %	Na, %	K, %	Rb, %	Ca, %	Sr, %
Gneiss	Comparison	—	2,20	3,77	0,0077	0,125	0,0175
	Additions	—	2,22	3,84	0,0074	0,130	0,0180
	Others	—	—	—	0,007 (s)	0,131 (c)	0,020 (s)
Gneiss	Comparison	—	2,57	3,52	0,0065	0,290	0,0084
	Additions	—	2,64	3,50	0,0070	0,280	0,0075
	Others	—	—	—	0,0070(s)	0,293(c)	0,0065 (s)
Granite	Comparison	0,0013	3,90	4,10	0,012	1 80	0,0120
	Additions	0,0014	3,80	4,00	0,011	1,80	0,0120
	Others	0,0010(s)	—	4,0	—	1,75 (c)	0,0130 (s)
Syenite	Comparison	0,0019	3,75	11,9	0,150	1,90	0,164
	Additions	0,0020	3,70	12,0	0,155	1,85	0,160
	Others	0,0020(s)	4,0 (c)	12,0(c)	0,17 (s)	2,00 (c)	—
Micro-cline	Comparison	0,0007	—	11,2	0,28	—	0,0022
	Additions	0,0007	—	11,3	0,29	—	0,0022
	Others	0,0009(s)	—	—	0,28 (s)	—	—

Notes: s) spectrographic method; c) chemical method.

TABLE 3

Taken γ / ml				Impurities, mg/ml			Found, γ / ml				Error, %			
Li	Rb	Sr	Ca	Na	K	Ba	Li	Rb	Sr	Ca	Li	Rb	Sr	Ca
0,80	1,50	1,33	15,6	0,3	0,4	0,2	0,85	1,55	1,36	15,4	+6,3	+3,3	+2,2	−1,3
2,40	1,50	1,33	1,56	0,3	0,4	0,2	2,30	1,55	1,29	1,51	−4,2	+3,3	−3,0	−3,2
4,80	3,00	6,65	3,12	0,5	0,4	0,3	4,80	2,90	6,51	3,2	0,0	−3,3	+2,1	+2,6
9,60	3,00	3,32	6,24	0,5	0,5	0,3	9,90	3,20	3,42	6,00	+3,1	+6,7	+3,0	−3,9
9,60	0,70	33,2	1,56	0,5	0,4	0,1	9,35	0,75	35,0	1,60	−3,0	+7,1	+5,4	+2,5
12,0	9,0	2,66	23,4	0,4	0,5	0,2	12,8	8,6	2,60	23,5	+6,4	−4,5	−2,3	+0,4
2,40	1,65	1,99	20,8	0,3	0,2	0,2	2,45	1,60	20,5	22,0	+2,1	−3,1	+3,0	+5,7
4,80	15,0	3,32	6,24	0,2	0,2	0,3	4,70	15,0	3,25	6,30	−2,1	0,0	−2,1	+1,0

TABLE 4

Rock	Method of determination	Li·10⁻⁴, %	Na, %	K, %	Rb·10⁻⁴, %	Ca, %	Sr, %
Granite G-1	Spectrographic	19; 23; 25 [16]			250 [16]		0,028 [16]
	Flame photometric	20 [10]; 24 [3]			205 [3]; 204 [10]		
	Isotopic dilution	—			215, 218 [17]		
	Neutron activation	—			221, 243, 254 [18]		
	Chemical	—	2,41 [16]	4,50 [16]	—	1,0 [16]	
	Author's results	20	2,43	4,30	202	0,97	0,029
Diabase W-1	Spectrographic	9, 9; 20 [16]			15; 20 [16]		0,029 [16]
	Flame photometric	14 [3, 10]			19; 25 [10]		
	Isotopic dilution	—			27; 29 [17]		
	Neutron activation	—			27; 29; 26; [18]		
	Chemical	—	1,50 [16]	0,53 [16]	—	7,9 [16]	—
	Author's results	9	1,57	0,54	26	8,1	0,031

SUMMARY

A method has been developed for the determination of the alkali and alkaline-earth elements in silicate rocks when the contents of these elements is not less than 0.001%.

A flame spectrophotometer with an air-acetylene burner, a monochromator, and a photomultiplier has been designed. Measurements were carried out on the basis of the following lines: Li 670.7 mμ, K 766.5 mμ, Na 588.9 mμ, Rb 780.0 mμ, Ca 549.8 mμ, and Sr 460.7 mμ.

Preliminary chemical treatment includes decomposition of the sample with hydrofluoric and perchloric acids, leaching the calcined precipitates with 2 N hydrochloric acid, and precipitating aluminum with ammonia. The experimental error does not exceed 5-6%.

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THE METHOD OF "IN SITU NASCENDI" REAGENTS

COMMUNICATION 2. THE USE OF DIOXANE DURING THE DETERMINATION OF CALCIUM AND STRONTIUM AS THEIR SULFATES*

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In our first communication [1] a description was given of the determination of the alkaline-earth metals by means of the method of "in situ nascendi" reagents using dimethyl sulfate which gradually gives SO_4^{2-} ions during hydrolysis. Separate determination of calcium and barium can be carried out by adding to the solution some glycerol, glucose, or sugar which form water-soluble, unstable complexes with the ions of the alkaline-earth metals. By adopting this technique the quality of the precipitate is improved as a consequence of the gradual appearance in solution of both SO_4^{2-}, and Ba^{2+}, and Ca^{2+} ions which arise during the dissociation of the unstable complexes with the hydroxy compounds. Willard et al [2, 3] who developed a method for precipitation in homogeneous solutions (or as we propose to call it the method of precipitation by "in situ nascendi reagents"), did not turn their attention to the significance of complexing agents, although in order to remove accompanying metals resort has often been made [4-8] to the addition of "masking" reagents. The part played by various "masking" agents, according to accepted ideas, reduces merely to the formation of more stable complexes by individual ions [2, 9-14]. We are of the opinion that the improvement in the form of the precipitation of the salt undoubtedly depends also on whether the ion to be precipitated is found in the form of a complex compound or not.

Addition of organic solvents (alcohols, acetone, etc) is usually recommended for determining the solubility of the precipitated salt. Nevertheless, in a number of cases of a similar type, reagents make it possible to prepare more suitable precipitates by forming complex compounds which are not very stable with the ion to be precipitated.

Modern organic chemistry and chemical industry have suggested many new solvents which have not yet found wide application in the practice of inorganic analysis. The present article contains some examples of the use of an active solvent of this type, namely dioxane.

Dioxane or diethylene ether $O=(CH_2-CH_2)_2=O$ is a liquid which boils at 101° and has a sp. gr. of 1.03; it is miscible with water and is a good solvent for organic materials. Dioxane can form unstable oxonium salts with strong acids. It forms with metal salts, mainly with halides, complex compounds which dissociate in aqueous solution ti a greater or lesser extent. Menshutkin [15, 16] as long ago as 1903 describe a number of such complexes. Thus, the halides of the alkali and alkaline-earth elements, and also some heavy metal salts form compounds —"etherates"— with dioxane. Later, a number of authors (Lynch [17], Bogardu [18], Weicksel [19], and Rheinbodt [20] et al) studied in detail the physicochemical properties of the compounds of the metal halides with dioxane.

In addition, dioxane decreases the solubility of various salts, thereby, exhibiting a salting out effect. Using these properties of dioxane, we used it in analysis of calcium and strontium. It was found that dimethylsulfate., in the presence of excess dioxane, precipitates dense, compact, fibrous precipitates of calcium and strontium sulfates from weakly hydrochloric acid or neutral solutions of calcium and strontium salts. (See fig.). The coagulation

* For communication 1, see [1].

A

B

A) Calcium sulfate precipitated from an aqueous solution of calcium chloride by means of dimethyl sulfate in the presence of dioxane (× 75);

B) Calcium sulphate, precipitated from a 75% alcoholic solution of calcium chloride by means of sulfuric acid (× 75).

of calcium sulfate and strontium crystals is related to the fact that dioxane forms soluble complexes with calcium and strontium chlorides. When a sufficient amount of sulfate ions appear, precipitates of calcium and strontium sulfates are formed.

Precipitation of Calcium Sulfate by Means of Dimethyl Sulfate in the Presence of Dioxane

Calcium sulfate can be crystallized in the form of its dihydrate, its semihydrate, or as the anhydrous form (anhydrite).

The question of the dehydration of the crystallohydrates of calcium sulfate has occupied many authors for a long time and the results obtained are very contradictory. These results relate mainly to synthetic preparations obtained from calcium salts and sulfuric acid, or to natural gypsum. Thus, Van't Hoff [21] who established the conditions for the changeover of the dihydrate into the semihydrate and the anhydrite, by changing the vapor pressure of the system, came to conclusion that up to 107° there exist all the varieties of calcium sulfate, while from 107 to 170° the semihydrate and anhydrite are the stable forms, at higher temperatures only modifications of the anhydrous form of calcium sulfate can exists. According to Betekhtin [22] and Millon [23] some varieties of the dihydrate may lose half a molecule of water as low as 80-90°, while other forms do not lose the water at this temperature, but lose one and a half molecules of water at 150°. According to the work of Zeidler, which Budnikov quotes [24], both natural as well as synthetic $CaSO_4 \cdot 2H_2O$ on heating in a current of air at 90-96° change into $CaSO_4 \cdot 0.5H_2O$. Chenston and Kundal, according to the same results [24], established that liberation of water from natural gypsum starts at a temperature as low as 40°. According to other results, significant loss of water may occur from the dihydrate even at normal temperatures as long as it is kept in a dry place. The work of Potylitsyn [25] showed that synthetic gypsum dried in a desiccator at 60-65° for several days changed into the semihydrate.

Budnikov [24] in summarizing the results of various researches, concluded that loss of water from the dihydrate of calcium sulfate starts within the temperature range 40 to 105°. At 107-128° gypsum loses only part of its water and is converted into the semihydrate. Dehydration starts at 110° in the case of some forms of gypsum, and is complete at 130°. Nevertheless, according to the work of Turuev [26] natural gypsum can change into the semihydrate at 82°; the author points out that under laboratory conditions, spontaneous decomposition of the semihydrate does not occur; the humidity of the air has a decisive effect on the stability of the semihydrate. Conversion of the semihydrate into anhydrite starts at 400°. Within the range 400 to 750° the

TABLE 1

Precipitation of Calcium by Dimethyl Sulfate in the Presence of Dioxane (weighed form $CaSO_4 \cdot 0.5H_2O$)

Calcium taken, mg	Calcium found, mg	Error	
		mg	%
21,00	21,24	+0,24	+1,1
37,05	37,19	+0,19	+0,4
52,50	51.35	−1,15	−2,1
61,75	60,03	−1,72	−2,1
86,45	87,14	+0,69	+0,8
123,50	124,96	+1,46	+1,1

TABLE 2

Precipitation of Calcium by Dimethyl Sulfate in the Presence of Dioxane (weighed form, $CaSO_4$)

Calcium taken, mg	Calcium found, mg	Error	
		mg	%
12,35	12,31	−0,04	−0,30
21,00	20,44	−0,56	−2,50
24,74	24,61	−0,13	−0,50
37,11	37,62	+0,51	+1,00
37,11	36,97	−0,14	−0,37
56,10	55,55	−0,55	−0,90
224,40	221,22	−3,18	−1,40
325,50	320,72	−4,78	−1,40

TABLE 3

Successive Precipitation of Barium and Calcium in Each Other's Presence

Cation det'd	Taken, mg	Found, mg	Error	
			mg	%
Ba^{2+}	13,95	13,81	−0,14	−1,0
Ca^{2+}	123,50	121,14	−2,36	−1,9
Ba^{2+}	32,60	32,48	−0,12	−0,30
Ca^{2+}	217,00	209,88	−7,12	−3,20
Ba^{2+}	40,55	40,90	+0,45	+1,1
Ca^{2+}	54,25	52,96	−1,39	−2,3
Ba^{2+}	48,00	48,34	−0,06	−0,1
Ca^{2+}	325,50	320,72	−4,72	−1,4
Ba^{2+}	40,60	40,43	−0,17	−0,4
Ca^{2+}	324,40	321,22	−3,18	−1,4

water is completely removed and anhydrous calcium sulfate is obtained.

In order to develop a gravimetric method of determining calcium, it is important to know the composition of the precipitated form and of the form in which it is to be weighed, when calcium is precipitated from aqueous solution by dimethyl sulfate in the presence of dioxane. The freshly precipitated form, as studies under the polarizing microscope showed, consists in the main of the semihydrate of calcium sulfate with small inclusions of the dihydrate. When this precipitate is filtered off, washed with alcohol and ether, and dried at 90-100° to constant weight, only the semihydrate is obtained. This was confirmed by repeated observations under the polarizing microscope, and also by the results of x-ray phase structural analysis*.

On drying the calcined precipitate to constant weight at 600-800° anhydrous calcium sulfate was obtained. Studies of this precipitate under the polarizing microscope showed that in the given instance there is formed the β-modification of anhydrous calcium sulfate; this was in complete agreement with the results of Ramsdell and Partridge [27]. This was also confirmed by the method of x-ray phase structural analysis.

Determination of Calcium

a. Weighed form $CaSO_4 \cdot 0.5H_2O$. A neutral or weakly hydrochloric acid solution containing 20-120 mg of calcium is diluted with water to 20-25 ml, 40-50 ml of dioxane is added and the solution heated to 60-70°, and 5 ml of dimethyl sulfate added immediately. (In order to cut down evaporation of the dimethyl sulfate, as indicated already [1], a round-bottom flask containing ice or cold water should be placed over the beaker).

The solution plus the precipitate which has separated out is heated on a water bath or left at 40-50° for 20-25 minutes. The precipitate is filtered through a No. 3 or No. 4 sintered glass crucible, and the filtrate carefully sucked through, the precipitate is washed 2-3 times with dioxane and then with alcohol and ether (it is sufficient to take 10 ml of wash liquor each time), care being taken to ensure as complete removal of filtrate as possible from the precipitate.

After completion of the washing air is drawn through the precipitate for a further 10 minutes. Crucible and precipitate are dried at 90° to constant weight; after cooling in a desiccator, the precipitate is weighed. The calcium is weighed in the form of $CaSO_4 \cdot 0.5H_2O$.

The conversion factor from $CaSO_4 \cdot 0.5H_2O$ to Ca is 0.2755 and to CaO is 0.3857.

Where necessary the dioxane can be recovered. It should be borne in mind that the vapors of dioxane are poisonous, so that experiments with this material should be carried out under a forced draft.

* The x-ray phase structural analysis of the precipitates prepared was carried out in the x-ray laboratory of the Institute of Chemical Reagents by E. A. Shuga, for which the authors to express their thanks.

Results of the determination of calcium by precipitation of the latter from aqueous dioxane solutions by means of dimethyl sulfate, with subsequent drying of the precipitate at 90° are given in Table 1.

b. Weighed form $CaSO_4$. After precipitating calcium with dimethyl sulfate and holding the precipitate at 40-50° for 20-25 minutes, the precipitate is filtered through a paper filter and washed 2-3 times with dioxane; the precipitate is dried as usual in a porcelain crucible, and then calcined at 600-800°.

From Tables 1 and 2 it is clear that both methods of precipitating calcium with dimethyl sulfate in the presence of dioxane give completely satisfactory results. Saving of time is considerable. It is possible to carry out to to three parallel determinations in one and half hours. The precipitates of calcium sulfate semihydrate and calcium sulfate anhydride obtained are very readily removed from the crucible in the form of compressed sheets, so that preparation of a crucible for further work presents no difficulty.

Determination of Calcium in the Presence of Barium

In the presence of glycerol, precipitation of calcium by dimethyl sulfate from aqueous dioxane solutions is slowed down considerably. This means that it is possible to determine barium and calcium successively as follows.

A neutral solution containing 13-50 mg of barium and 50-300 mg of calcium in the form of chlorides is diluted with water to 70-80 ml, and 5-15 ml of glycerol added, the solution is heated to 60-70° and 5 ml of dimethyl sulfate added dropwise. Heating is continued for another 30 minutes. The precipitated barium sulfate is filtered off through an ashless filter and washed, and is finally calcined at a red heat, or it is filtered through a No. 4 sintered glass crucible and dried at 140°. It is cooled in a desiccator and weighed.

TABLE 4

Determination of Calcium in the Presence of Aluminum and Iron Chlorides, and Hydrochloric Acid (52.50 mg Ca taken).

Foreign salts taken, mg	Ca found, mg	Error	
		mg	%
$FeCl_3$ 180 HCl 2360	51,96 51,02	—0,54 —1,48	—1 —2
$FeCl_3$ 180 $AlCl_3$ 100 HCl 2360	50,64	—1,86	—3

TABLE 5

Composition of the Limestone and Clays

Loss on calcining	SiO_2, %	Fe_2O_3, %	Al_2O_3, %	MgO, %
42,89	1,38	0,68	—	0,30
43,29	1,72	0,21	0,17	1,09
39,41	19,30	4,55	3,10	2,25
—	—	4,57	15,03	4,09

The filtrate and the wash water are evaporated to 20-25 ml, 50 ml of dioxane is added and the solution heated on a water bath to 60-70°. After 15-20 minutes the calcium sulfate is precipitated. The procedure outline above is then followed.

Results for the successive determination of barium and calcium by means of dimethyl sulfate from aqueous glycerol and aqueous dioxane solutions are given in Table 3.

For simplifying and cutting down the time of an analysis, the filtrate can be transferred to a standard flask and precipitation of calcium carried out on an aliquot of this solution.

Determination of Calcium in the Presence of Aluminum, Iron, Ammonium, and Hydrochloric Acid.

As experiment showed, determination of calcium in the presence of large amounts of the chlorides of aluminum, iron, and ammonium is impossible, since the aqueous dioxane solutions separate into layers and the calcium sulfate is not precipitated. When the amount of iron and aluminum chlorides is twice that of the calcium, and the amount of hydrochloric acid is 150 times as much, calcium sulfate is precipitated (a precipitate appears 40-50 minutes after addition of the dimethyl sulfate), but the results obtained are high. Correct results are obtained after reprecipitation. The following procedure is adopted. The calcium sulfate precipitate obtained is filtered through a fine filter paper, and, without washing it, the precipitate is returned to the beaker in which precipitation was first carried out. The precipitate is dissolved in 2 ml of concentrated hydrochloric acid on heating, and the solution filtered; the filter is carefully washed with hot water. The filtrate obtained is diluted to 20-25 ml with water and 50 ml of dioxane added, reprecipitation is then carried out with dimethyl sulfate.

TABLE 6

Determination of Calcium in Limestone and Clay by Means of Dimethyl Sulfate in the Presence of Dioxane

Sample	CaO found by the oxalate method, %	CaO found by the dimethyl sulfate-dioxane method, %	
		Ca weighed in the form $CaSO_4$	Ca weighed in the form $CaSO_4 \cdot 0.5H_2O$
Limestone	52,72	52 20	54,37
"	48,96	47,49	48,63
"	34,91	34,26	32,54
Clay	34,85	31,30	
"	12,56	11,32	

TABLE 7

Precipitation of Strontium with Dimethyl Sulfate in the Presence of Dioxane

Sr taken, mg	Sr found, mg	Error	
		mg	%
19,64	19,46	—0,18	—0,90
29,79	30,19	+0,40	+1 30
39,72	40,11	+0,39	+1,00
49,10	49,50	+0,40	+0,80
79,56	78,28	—0,28	—0,33

Results for the determination of calcium in the presence of aluminum, iron, and hydrochloric acid are given in Table 4.

Determination of Calcium in Limestone and Clay

The method developed for the determination of calcium was applied to samples of limestone and clay readily soluble in hydrochloric acid; the composition of these materials is given in Table 5.

A sample of limestone or clay (about 1 g) is placed in a 100-150 ml breaker and moistened with 5-10 ml of water, the suspension is heated and hydrochloric acid (1:1) added in small portions until solution is complete. A large excess of hydrochloric acid should be avoided; usually 15-20 ml of acid is sufficient. The solution obtained is diluted to 60-70 ml with water, and is then heated to the boil and filtered through a fine filter paper using paper pulp; the filtrate is collected in a 250-300 ml standard flask. The insoluble residue remaining on the filter is washed 5-6 times hot water + HCl. After cooling, the filtrate is made up to mark with water. 20-25 ml of this solution is then pipetted into a 100-150 ml beaker and heated to 60-70°; 50 ml of dioxane is added followed by 5 ml of dimethyl sulfate. The solution is heated on a water bath for 20-30 minutes. The precipitate which separates out is filtered either through a fine filter paper or through a No. 3-4 sintered glass crucible. In the first instance the precipitate is washed two-three times with dioxane, dried, and then calcined at 600-800°. The form in which the calcium is weighed in this case is $CaSO_4$. In the second instance the precipitate is washed twice with dioxane, and then with alcohol and ether, using 10-12 ml portions; air is then sucked through the precipitate for 10-15 minutes, and the precipitate dried to constant weight at 90°, calcium is weighed in this case as $CaSO_4 \cdot 0.5H_2O$.

Calcium was determined in parallel on the same samples using the classical method [28].

Results for the calcium determinations are given in Table 6.

The method described can be recommended for the rapid analysis of natural samples. The method gives satisfactory results, and is simple and convenient to carry out.

Determination of Strontium. Strontium is usually determined either as the sulfate which is precipitated from a 50% alcoholic medium, or as the oxalate also from alcoholic media. The precipitate obtained is thereupon calcined and either the sulfate or the oxide is obtained. Nevertheless, it is well known [29] that determination of strontium even in the absence of other ions is very complicated and takes a long time.

It was found that dimethyl sulfate in the presence of dioxane, precipitates strontium from aqueous solutions of its salts, in the form of a coarse crystalline precipitate of strontium sulfate.

A neutral solution containing from 20 to 80 mg of strontium in the form of its chloride is diluted with water to 25 ml, 50 ml of dioxane is added and the solution heated to 60-70°; 5 ml of dimethyl sulfate is then added with stirring. After several minutes a crystalline precipitate which readily separates out starts to form. The mixture is heated on a water bath for 15-20 minutes, and, after cooling, the precipitate is filtered through a fine filter; the precipitate on the filter paper is washed 3-4 times with dioxane (10-12 ml each time). The filter paper and precipitate are dried in a crucible and then calcined to constant weight. Strontium is weighed as $SrSO_4$.

SUMMARY

The analytical properties of precipitates can be improved by using the method of "in situ nascendi" reagents. The masking agents present during precipitation, do not merely suppress precipitation of accompanying metals, but also improve the form of the crystals of the salt precipitated. The reason for this is that some of the ions are found in the form of a complex which gradually dissociates.

Methods have been developed for determination of calcium and strontium as their sulfates, the latter being precipitated from aqueous dioxane solutions by means of dimethyl sulfate. Dioxane forms unstable soluble complexes with calcium and strontium chlorides, and depresses the solubility of the sulfates formed. A rapid method is described for determining calcium in the form of calcium sulfate semihydrate or in the form of anhydrous calcium sulfate in the presence of barium, aluminum, iron, and ammonium salts, and also in natural limestone and clay.

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THE USE OF COMPLEXON III (EDTA) FOR SEPARATING BARIUM, STRONTIUM, AND CALCIUM

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In the work described here, the separation of barium, strontium, and calcium as their sulfates in the presence of EDTA (ethylenediaminetetraacetic acid) was studied, using radioactive indicators. The possibility of such a separation arises on the basis of the following considerations. The stability of the complex compounds of the alkaline-earth metals with ethylenediaminetetraacetic acid differs. According to Schwarzenbach's results [1] the reciprocals of the logarithm of the instability constants of these complexes are 7.76 for Ba, 8.63 for Sr and 10.59 for Ca. The solubility of the sulfates of these metals decreases in the same order. The stability of the complexonates of Ba, Sr, and Ca is so great in an alkaline medium, that not even barium is precipitated as sulfate. On decreasing the pH the stability of the complexonates decreases, and the concentrations of the metal ions in solution increases. It is to be expected that on gradually acidifying a solution containing EDTA and SO_4^{2-} ions, $BaSO_4$ will be first precipitated, since the stability of barium complexonate and the solubility of barium sulfate are less than those for strontium and calcium, and this means that the concentration of ions exceeding the solubility product will be reached sooner. Should precipitation start, then it should proceed quantitatively, since deposition of $BaSO_4$ decreases the concentration of Ba^{2+} in solution, and displaces the equilibrium towards breakdown of the complex. On decreasing the pH further, precipitation of $SrSO_4$ should occur, while calcium which gives a more soluble sulfate and a more stable complex, will remain in solution at this pH.

The results obtained confirmed, in the main, these assumptions.

Experimental Technique. The strontium radioactive indicator used was Sr^{90}, which is in equilibrium with Y^{90}. Since, from a solution containing EDTA, yttrium is not trapped during precipitation of strontium and barium, measurements could be carried out in two ways: 1) by measurements of the activity of the solution on a β-counter on the basis of the increase or breakdown of Y^{90}; 2) measurements of β-activity of Sr^{90} in the precipitates immediately after precipitation, using a torsion counter. We used both these methods.

Ca^{45} was used as the indicator for calcium. The activity of the precipitates was measured by a torsion counter on a type B-2 setup. All the chemical operations were carried out in centrifuge tubes. The total volume amounted to 5-8 ml. Precipitates were separated by centrifugation. The amount of precipitated or coprecipitated element was determined on the basis of activity measurements.

Precipitation of Strontium in the Form of Sulfate. According to Ballczo and Doppler [4] it is impossible to precipitate strontium sulfate quantitatively from solutions containing EDTA; we investigated this point.

Strontium was precipitated at pH about 5 (appearance of the rose color of methyl red), which corresponded to the beginning of this process. To 1 ml of a solution of strontium nitrate containing 10 mg of strontium, was added the radioactive indicator (Sr^{90}), excess of EDTA (2 ml of a 10% solution), a few drops of methyl red, and ammonia until a yellow color was obtained; 2 ml of 10% ammonium sulfate was finally added. The solution was heated on a water bath and carefully acidified with dilute HCl just to the appearance of the rose color of the indicator. The precipitate which separated out was centrifuged and washed twice with 2 ml of wash liquor (100 ml of water, 1 g ammonium sulfate, 1 g of EDTA, and acid to the rose color of methyl red). The activity of the precipitate was measured on a torsion counter. For removing the strontium remaining in solution after the precipitation, 10 mg of strontium in the form of nitrate was added to the solution and then precipitated. The

TABLE 1

Precipitation of Strontium as Sulfate From a Solution Containing EDTA, at pH about 5 (10 mg Sr taken)

Activ. of the precipitates		% Sr in	Notes
after 1st ppt.	after 2nd ppt.	solution	
17060	400	2,3	Centrifugated immediately
16600	940	5,4	
17910	364	2,0	
18800	508	2,6	Centrifugated after 2 hours
17520	316	1,8	
18490	340	1,8	
20110	333	1,6	Centrifugated after 24 hours
20970	353	1,7	
22617	367	1,6	

activity of the second precipitate, expressed as a fraction of the total activity of the first and second precipitates, gives the percentage strontium remaining in solution after the first precipitation. It is clear from Table 1 that even after 2 hours, precipitation occurs to the extent of 97.9% on an average, while on leaving the precipitate overnight precipitation increases to 98.4%. The amount of strontium remaining in solution thereupon is 0,16 mg. Precipitation to this extent can be regarded as fully satisfactory. The incomplete precipitation of strontium sulfate in the work of Ballczo and Doppler [4] can presumably be attributed to the enhanced solubility of $SrSO_4$ in the presence of excess foreign salts added in order to attain the necessary pH [2,3].

Separation of Barium and Strontium.

Ballczo and Doppler [4] showed that separation of barium from strontium is most conveniently carried out by precipitating barium with chromate; we were, however, interested in the sulfate method of separation.

Our first experiments, in agreement with the results of Ballczo and Doppler [1] showed that, when only one precipitation was carried out, an appreciable amount of strontium was trapped by the barium sulfate; in future experiments therefore reprecipitation was carried out.

TABLE 2

Separation of Barium and Strontium by Precipitation of $BaSO_4$ from a Solution Containing EDTA, pH about 8.

Taken, mg		Ba : Sr	Activ. of $BaSO_4$		Sr trapped	
Ba	Sr		of the solution	total	in %	in mg
10	10	1 : 1	205	16330	1,3	0,13*
10	10	1 : 1	303	19270	1,6	0,16*
10	10	1 : 1	374	17530	2,2	0,22*
10	10	1 : 1	38	18210	0,2	0,02
10	10	1 : 1	72	15730	0,5	0,05
10	10	1 : 1	40	16980	0,25	0,025
10	1	10 : 1	42	16820	0,25	0,0025
10	1	10 : 1	2	16930	0,01	0,0001
10	1	10 : 1	38	15530	0,25	0,0025
5	50	1 : 10	0	12850	0	0
5	50	1 : 10	0	13830	0	0
5	50	1 : 10	20	15740	0,13	0,065
10	10^{-2}	1 : 1000	22	15700	0,15	$1,5 \cdot 10^{-5}$
10	10^{-2}	1 : 1000	33	16520	0,2	$2 \cdot 10^{-5}$
10	10^{-2}	1 : 1000	0	14210	0	0

* Without reprecipitation

The work was carried out as follows. To the solution (1-2 ml) containing $BaCl_2$ and Sr nitrate was added the radioactive indicator (Sr^{90}), excess of EDTA, ammonia until its odor was perceptible, and 1-2 ml of 10% ammonium sulfate solution. The solution was heated on a water bath; during this stage, as a result of volatilization of the ammonia, the pH decreased slowly and uniformly. Precipitation of $BaSO_4$ started at a pH of about 8. Further heating on a water bath is perfectly safe, since the drop in pH which thereupon occurs is not sufficient to lead to precipitation of strontium sulfate. This method of lowering the pH is the most convenient technique; on lowering the pH by adding acid, the drop in the pH in individual parts of the solution is too sharp and leads to a partial deposition of strontium sulfate with subsequent trapping with the barium.

After precipitation of the $BaSO_4$ the precipitate was centrifuged and washed twice with 2 ml of wash liquor (100 ml water, 1 g ammonium sulfate, 1 g EDTA, and ammonia to a weak odor). The precipitate was dissolved in an ammoniacal solution of EDTA and the precipitation repeated in the same way. After centrifuging and washing, the precipitate was again dissolved in the ammoniacal solution of complexon, and the solution transferred to a vessel in order to measure its activity. The amount of strontium which was coprecipitated with the barium was determined by comparing the activity of the dissolved barium sulfate and the activity of the solution left after centrifuging. Measurement of the activity of the solutions was carried out on a β-counter on the basis of the increase or breakdown of Y^{90}. The results obtained for various ratios of barium and strontium are given in Table 2. They showed that even after only one precipitation (without reprecipitation) the amount of strontium

TABLE 3

Separation of Strontium and Calcium by Precipitation of Strontium as the Sulfate from a Solution Containing EDTA, pH about 5

Taken, mg		Sr : Ca	Activity		Ca trapped	
Sr	Ca		$SrSO_4$	of the standard	in %	in mg
10	1	10:1	36	7 780	0,5	0,005
10	1	10:1	87	7 780	1,2	0,012
10	1	10:1	40	7 780	0,5	0,005
10	10	1:1	18	7 780	0,25	0,025
10	10	1:1	10	7 780	0.15	0,015
10	10	1:1	20	7 780	0,3	0,03
5	50	1:10	20	7 780	0,3	0,15
5	50	1:10	23	7 780	0,3	0,15
5	50	1:10	28	7 780	0,4	0,2

occluded was only 1.3-1.6% of the amount present (Ba : Sr = 1 : 1); in those cases where reprecipitation was carried out, the amount of strontium trapped did not exceed 0.5% for all the ratios of barium to strontium studied. This means that this method permits the quantitative separation from barium of even micro amounts of strontium. The whole process presents no difficulties and takes 1.5-2 hours.

Separation of Strontium and Calcium. During the separation of the alkaline-earth elements, separation of strontium from calcium causes the greatest difficulties; accordingly, a study of this question is of special interest. The results of the work carried out during the present investigation on the precipitation of strontium sulfate led to the possibility of separating these elements in the form of their sulfates in the presence of EDTA. This possibility was investigated for the following ratios of strontium to calcium: 1:1, 1:10, and 10:1. The experimental technique was as follows. To a solution containing strontium nitrate and calcium chloride was added some radioactive indicator (Ca^{45}), excess EDTA, a few drops of methyl red, ammonia to the yellow color of the indicator, and 2 ml of a 10% solution of ammonium sulfate. The strontium sulfate was precipitated by the method described above. The $SrSO_4$ precipitate was centrifuged 2 hours after precipitation. The amount of calcium coprecipitated with the strontium was determined by comparing the activity of the strontium sulfate obtained, and that of a standard which was prepared by mixing exactly the same amounts of radioactive indicator and strontium sulfate as in the test solution. The results obtained (Table 3) show that it is possible to separate strontium and calcium by one precipitation of $SrSO_4$ (without reprecipitation) from a solution containing EDTA. The amount of calcium trapped by the strontium sulfate did not exceed 0.5% of that present for most cases. Only for very low calcium contents did this figure increase to 1.2%; nevertheless, even in this case the error only amounted to 0.01 mg. It should be pointed out that in those cases where the calcium content is considerably greater than that of strontium, even an insignificant amount of calcium present as an impurity can lead to an appreciable error in the determination of strontium. In such cases it is essential to reprecipitate the $SrSO_4$.

SUMMARY

Using the method of radioactive indicators, a study has been made of the possibility of separating barium, strontium, and calcium as their sulfates in the presence of EDTA. In agreement with the results of Balicz0 and Doppler [4] it has been established that barium can be quantitatively separated from strontium by precipitating $BaSO_4$ from a solution containing EDTA at a pH of about 8, with a subsequent reprecipitation. The amount of strontium coprecipitated with barium does not exceed 0.5% of that present. Despite what the authors indicated state, it has been established that strontium can be quantitatively precipitated as the sulfate from a solution containing EDTA. A method is suggested for separating strontium and calcium in which strontium sulfate is precipitated from a solution containing EDTA at a pH of about 5. The amount of calcium coprecipitated does not exceed 1.2 % of that present.

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THE APPLICATION OF TRIHYDROXYFLUORONE DERIVATIVES IN PHOTOMETRIC ANALYSIS. DETERMINATION OF SCANDIUM

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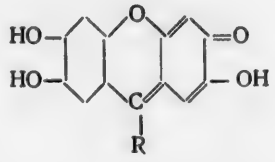
Seeking color reactions for scandium which could be used as the basis of a photometric method of determining this element, we studied some compounds of the orthohydroxyquinone group as potential reagents, individual representatives of this group having already found application in analytical chemistry (chloranilic acid, phenylfluorone, hematein, etc.). In the first instance we tested various derivatives of 2,3,7-trihydroxy-6-fluorone, substituted in the 9-position, whose reactivity towards various metals has been established in the work of Duckert and Gillis et al [1-3], and also in the work carried out in our laboratory [4,5].

Ortho Hydroxyquinones as Reagents for Scandium

Trihydroxyfluorone derivatives  were synthesized from triacetylhydroxyquinone

and the respective aldehyde. 0.001 M weakly acid alcoholic solutions were used as reagents; the solutions were prepared by dissolving the requisite amount of compound on moderate heating in 100 ml of 96% ethanol to which 0.5 ml of 6 N HCl has been added. The original scandium solution (1 mg/ml) was prepared by dissolving pure scandium oxide in 1 N sulfuric acid and then diluting with water. This stock solution ,which was 0.01 N with respect to sulfuric acid, was dilute with water to obtain a working solution with the desired scandium content. The reactions were carried out in the presence of a buffer solution within the pH range 1 to 8. The buffer solutions used did not contain any possible precipitants or complexing agents for scandium: chloride, hydrogen phthalate, acetate, glycol, or veronal.

Procedure. To 1 ml of scandium solution was added buffer solution so as to get the requisite pH, the solution was then diluted with water to 4.8 ml and 0.2 ml of reagent solution added. The results obtained are given in Table 1.

Of other compounds containing the orthohydroxyquinone group of atoms, the following compounds were taken: chloranilic acid, hematein, individual representatives of the hydroxy derivatives of the phthaleins, and also compounds of the oxazine group (gallocyanine), and azo derivatives of pyrocatechol which can react in a tautomeric form. The reactions with these compounds were carried out in the same way as with the trihydroxyfluorone derivatives. The results obtained are given in Table 2.

All the reactions described above are not selective for scandium. In a strongly acid medium it is known that trihydroxyfluorone derivatives react with germanium, tin (IV), zirconium, niobium, molybdenum etc.. On lowering the acidity to a pH of 3-7, elements of the third group of the periodic system begin to react: aluminum, gallium, indium, yttrium, and the rare-earths, and also iron (III), thorium, etc.. The selectivity of the other

TABLE 1

Reactions of Scandium with Trihydroxyfluorone Derivatives

Compound number	R	Color of the control solution	Color in the presence of Sc	Optimum pH	Limit of identification, γ
I	Methyl	Yellow	Rose	5,5	1
II	Trichloromethyl	»	»	5; 7,6	0,5
III	Propyl	»	Raspberry	5,6	0,1
IV	Phenyl	»	Rose	7,6	0,2
V	2-Hydroxyphenyl	»	Raspberry	5	0,1
VI	4-Hydroxy-3-methoxyphenyl	»	»	5	0,3
VII	4-Methoxyphenyl	»	Rose	5,6	0,2
VIII	2-Hydroxyl-1-naphthyl	»	»	5	0,3
IX	2-Nitrophenyl	Rose	Raspberry	4	0,3
X	3-Nitrophenyl	Yellow	Rose	7,6	0,3
XI	4-Nitrophenyl	»	»	7.6	0,3
XII	2,4-Dinitrophenyl	Orange	Raspberry	5,6	0,4
XIII	2-Hydroxy-3-nitrophenyl	»	»	5,6	0,2
XIV	4-Hydroxy-3-methoxy-6-nitrophenyl	Yellow	Red	5,6	0,2
XV	4-Dimethylaminophenyl	»	Rose	7,6	1
XVI	2-Methoxy-3,4-methylenedihydroxy-6-ethyl-β-methylaminophenyl	»	»	5	1
XVII	2,4-Disulfophenyl	»	»	5,6	1

TABLE 2

Reactions of Scandium with Other Ortho Hydroxyquinones

Compound	Color of control solution	Color in the presence of Sc	Optimum pH	Limit of identification γ
Chloranilic acid	Very pale lilac	Lilac	5,6	10
Hematein	Yellow	Rose	5	5
Gallein	»	»	5	1
Cerulein	Dirty violet	Brownish green	5,6	20
Gallocyanine	Blue	Rose	5,6	2
p-Nitrobenzene azopyrocatechol	Yellow	Rose	5,6	1
Stilbazo	Yellow	Rose	5,6	25

orthohydroxyquinones tested is approximately the same. In order to enhance the selectivity of the reaction the technique of masking interfering elements was adopted (aluminum, gallium, indium, iron, yttrium, lanthanum, cerium, zirconium, and thorium). Fluorides, sodium, citrate, oxalate, and pyrophosphate, ascorbic acid, EDTA, diketones and ketoalcohols, sugar, and some other materials, as well as mixtures of these, were tested as masking agents. Only acetylacetone masked all the elements tested, with the exception of iron, when the reagent used was 9-propyltrihydroxyfluorone. 0.1 ml of acetylacetone was sufficient for masking 5 γ of each of the elements listed above, without decreasing the sensitivity of the reaction for scandium.

It is thus clear that all the compounds tested with the orthohydroxyquinone group react with scandium. They do not give fluorescent reactions with scandium. The most sensitive reagents are 2, 3, 7-trihydroxy-6-fluorone derivatives; of these the most sensitive reagent for scandium, with respect to sensitivity and specificity (in the presence of acetylacetone), is 9-propyl-2,3,7-trihydroxy-6-fluorone (henceforth called propylfluorone). A comparison of the absorption curves of solutions of the compounds studied and of their complexes with scandium showed that propylfluorone is the most suitable for the spectrophotometric determination of scandium, since the superposition of the absorption curves of the reagent itself and of the complex with scandium least when this reagent is used. Another reagent which is equal in sensitivity to propylfluorone is o-hydroxyphenyltrihydroxyfluorone; nevertheless this compound is not so selective as propylfluorone, and does not permit masking of interfering elements without simultaneous masking of scandium. We chose propylfluorone for the quantitative determination of scandium.

Effect of pH. Propylfluorone in weakly acid or neutral media (pH 3-7) forms a red compound with scandium ions, this compound being precipitated when the scandium content is high.

Solutions of this compound are stabilized by gelatin. Weakly acid, dilute solutions, of propylfluorone have a yellow color with a yellowish-green fluorescence. In Fig. 1 is shown effect of pH changes on color development The solutions were 4×10^{-5} M with respect to propylfluorone and 12×10^{-5} M with respect to scandium. In order to stabilize the solutions, 0.5 ml of a 1% gelatin solution was added for a total volume of 25 ml; this was done in all subsequent experiments. The optical density was measured in a Pulfrich photometer using a 10 mm cell, water was the reference solution, and measurements were carried out at 530 mμ 30 minutes after preparing the solutions. As the curve shows, the maximum color develops at pH 5.6. At pH greater than 6 the optical density of solutions of the reagent increases sharply.

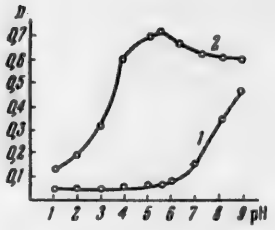


Fig. 1. Relation between color intensity and pH.: 1) reagent; 2) scandium complex.

Absorption curves of solutions of the reagent and of the complex, measured on a SF-4 spectrophotometer are shown in Fig. 2. The solutions were 2×10^{-5} M with respect to propylfluorone, and, in the case of the complex, 6×10^{-5} M with respect to scandium. Optical density measurements were carried out in a 5 mm cell against water, and were made 10 minutes after preparing the solutions. Maximum light absorption by reagent solution is observed at 480 mμ, while maximum light absorption by the complex is observed at 510 mμ. For this work it is convenient to use a light filter with maximum transmission at 530 mμ where the absorption of the complex is still high enough, while the reagent only absorbs to a small extent.

Composition of the Complex. In order to establish the molar ratio of propylfluorone to scandium in the complex, the Ostromyslensky-Job method, and the method of molar ratios [6, 7] were used.

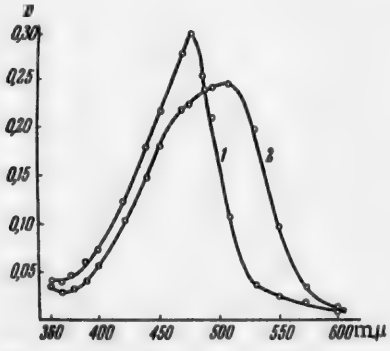


Fig. 2. Absorption curves: 1) reagent 2) scandium complex.

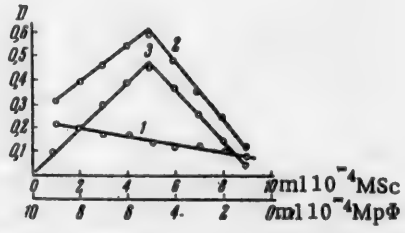
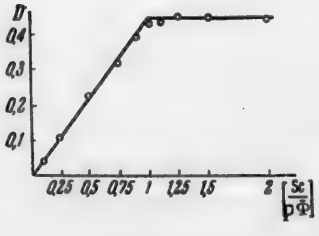
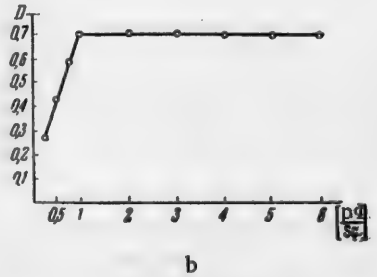


Fig. 3. Method of continuous changes: 1) reagent; 2) experimental results; 3) corrected results.



a



b

Fig. 4. Method of molar ratios: a) propylfluorone concentration constant; b) scandium concentration constant.

For the continuous-change method, the solutions used ranged from 0.4×10^{-5} to 3.6×10^{-5}M with respect to scandium, and from 3.6×10^{-5} to 0.4×10^{-5}M with respect to propylfluorone. Optical density measurements were carried out in a 10 mm cell against water, measurements were made at 530 mμ 2 hours after preparing the solutions. Measurements after 3, 4, and 5 hours have the same values for the optical density. Results of these measurements are given in Fig. 3.

Experiments were carried out by two variants for the molar ratio method: a) the propylfluorone concentration was kept constant at 2×10^{-5}M while the scandium concentration was varied from 0.1×10^{-5} to 4×10^{-5}M; b) the propylfluorone concentration was changed while the scandium concentration was kept constant. A correction was applied for the light absorbed by excess propylfluorone, the correction being determined by measuring the optical density of the corresponding solutions in the absence of scandium. The results obtained are given in Fig. 4a and 4b.

As is clear from Fig. 3, 4a, and 4b, the experimental results for both the optical methods indicate that only one complex is formed under the conditions used, and that this complex has a molar ratio of scandium to reagent of 1:1.

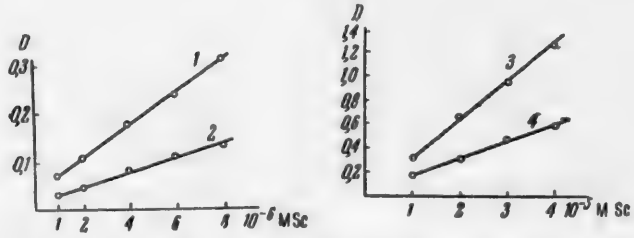


Fig. 5. Relation between optical density and scandium concentration. 1) 20 mm cell; 2) and 3) 10 mm cell; 4) 5 mm cell.

TABLE 3

Determination of the Equilibrium Constant ($t°=20°$; $l=10$ mm; standing time 2 hours).

Expt. No.	$C_{Sc} \times 10^5$	$C_{Sc}=C_{H\Phi}$		$C_{Sc}<C_{H\Phi}$		K'
		$C_{H\Phi} \times 10^5$	E	$C_{H\Phi} \times 10^5$	E_{max}	
1	1	1	0,31	6	0,34	$1,10 \cdot 10^7$
2	2	2	0,60	6	0,63	$1,90 \cdot 10^7$
3	3	3	0,88	6	0,92	$1,26 \cdot 10^7$
				Mean		$1,42 \cdot 10^7$

On the basis of the results obtained, and also on the assumption that the reactive group of atoms in propylfluorone is the orthohydroxyquinone group, the structure of the scandium complex can be regarded as similar to the structure of the phenolfluorone complex of antimony [4].

Equilibrium Constant. For calculating the apparent equilibrium constant of the reaction $ScO^+ + H\Phi \rightleftharpoons ScO + H^+$ the same method was adopted as that used for calculating the equilibrium constant of the reaction for the formation of antimony phenylfluoronate [4]. Calculations were made on the basis of the formula $K' = x/(c-x)^2$ if we let $x = Ec/E_{max}$ where x is the equilibrium concentration of the complex in solution, c is the total concentration of scandium in solution, E is the optical density for a stoichiometric ratio of scandium to propylfluorone and E_{max} is the optical density when excess propylfluorone is present. Results of these experiments are given in Table 3.

The equilibrium constant was also calculated by the Schaeppi-Treadwell method [8] from the results obtained during a study of the composition of the complex by the continuous change method (Fig. 3). At the point corresponding to the ratio Sc:H Φ= 1:1, the optical density was 0.44. The intersection point for the composition curves corresponded to an optical density of 0.46. The equilibrium constant of the reaction calculated from these results is 2.05×10^{7}.

The high value of the equilibrium constant indicates that the propylfluorone complex of scandium is highly stable. This constant can be used for calculating the requisite excess of reagent for the photometric determination of scandium; calculations show that in order to complex 99% of scandium as the colored complex it is sufficient to use a twofold excess of the reagent this was confirmed experimentally.

The molar extinction coefficient was determined for a wavelength of 530 mμ. Experiments were carried out for different scandium concentrations ($1-3 \times 10^{-5}$M) and a constant propylfluorone concentration (6×10^{-5}M), so that the ratio of their concentrations varied from 1:2 to 1:6. The mean value of the molar extinction coefficient was found to be 32,000.

When excess propylfluorone is used, and the pH is 5.6, the color reaches a maximum in as little as 5 minutes and does not change in the course of several hours.

Conformation to Beer's Law. In order to establish whether or not solutions of scandium propylfluoronate follow Beer's Law, the optical density of solutions with scandium concentrations ranging from $1 \times 10^{-6} - 8 \times 10^{-6}$M and $1 \times 10^{-5} - 4 \times 10^{-5}$M was measured. The concentration of propylfluorone was correspondingly 2×10^{-5} and 8×10^{-4}. Measurements were carried out relative to the same solution free from scandium. The results obtained are given in Figs. 5a and 5b, from which it is clear that, within the limits studied, the relation between color intensity and scandium concentration is linear. On increasing the scandium concentration above 5×10^{-5}M, the optical density of the solutions obtained is too high for measurement.

TABLE 4

Determination of Scandium in the Presence of Other Elements (3γ of Sc taken, 0.1 ml of acetylacetone added)

5γ of each metal added	Sc found, in γ
Al	3,1
Y	3,0
La	3,0
Ce	2,9
Th	3,0

Recommended Method for Carrying out the Determination. Into a 26 ml standard flask is introduced 1-10 ml of a weakly acid (not more than 0.005 N acid) test solution, so that after dilution to the mark, the scandium concentration lies within the limits 1×10^{-6}M (0.045γ Sc/ml) to 8×10^{-6}M (0.38γ Sc/ml). 0.5 ml of a 1 gelatin solution and 5 ml of a 0.003% solution of propylfluorone is added. The contents of the flask are then mixed and made up to the mark with an acetate buffer whose pH is 5.6, the solution is mixed again and then left for 10 minutes. The optical density is measured at 530 mμ relative to a control solution, in a 20 mm cell.

For determining the scandium concentration within the limits 0.4γ/ml to 2γ/ml, 2 ml of a 0.03% solution of propylfluorone is taken, and the optical density measured in a 5 or 10 mm cell. The order in which the solutions are added is the same.

Color intensity can also be measured visually by the method of standard series, or by using a colorimeter with a light filter e. g, the KOL-1M colorimeter

The 0.003% solution of propylfluorone should be prepared from the 0.03% solution by dilution with ethanol.

Table 4 contains results obtained during the determination of scandium in the presence of some interfering elements. The experiments were carried out as described above, but 0.1 ml of acetylacetone was added to the solutions.

SUMMARY

Compounds containing the orthohydroxyquinone group give color reactions with scandium. 2, 3, 7-Tri - hydroxy-6-fluorone derivatives are the most sensitive reagents. 9-Propyltridhydroxyfluorone permits detection of scandium at a dilution of $1:5 \times 10^{7}$, and is suitable for the photometric determination of 0.04γ/ml of scandium. Solutions of the scandium complex conform to Beer's law.

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AN INDIRECT PHOTOMETRIC DETERMINATION OF CYANIDE BY MEANS OF DIVALENT MERCURY AND DYPHENYLCARBAZONE

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We have developed a method for the direct photometric determinations of cynanide which is based on the color reaction of divalent mercury ions with diphenylcarbazone. The hydrogen cyanide liberated is absorbed by a solution of mercuric chloride. Only that part of the divalent mercury which has not reacted with cyanide reacts with diphenylcarbazone. The method is similar to one developed earlier with p-dimethylaminobenzylidenethiocyanate [1,2]. Divalent mercury ions, under the appropriate conditions, react with diphenylcarbazone to form a colloidal solution with a violet color. Diphenylcarbazide gives exactly the same color, since it is readily oxidized to diphenylcarbazone by atmospheric oxygen [3-6]. During a study of the reaction of both these reagents with divalent mercury, Alekseev [7] concluded that diphenylcarbazone is the most suitable reagent for the photometric determination of divalent mercury, since it can be obtained in a purer form, while the color developed is more stable. The reaction between divalent mercury and diphenylcarbazone is more sensitive than and is not so dependent on the experimental conditions, as the reaction of mercury with p-dimethylaminobenzylidenethiocyanate. In this respect therefore the new method is better than the one suggested previously.

Apparatus and Reagents. 1. Universal Coleman Spectrophotometer, Model 14, cell 14-307.

2. Conway Diffusion Apparatus (Microchemical Specialties) 172-A. Packing grease: vaseline + paraffin (1:2), m.p. 40°.

3. Approximately 0.1 M potassium cyanide. The molarity of the solution was determined by the usual method [8]. A solution with the requisite concentration was prepared prior to use by dilution.

4. A saturated aqueous solution of tartaric acid.

5. Buffer solution (pH 4.00). 800 ml of 0.2 M acetic acid was mixed with 200 ml of 0.2 M sodium acetate.

6. 1% alcoholic solution of diphenylcarbazone. The solution was filtered after standing overnight.

7. Mercuric chloride solutions. An aliquot of salt sufficient to give a solution with a concentration of 500 γ of Hg^{2+}/ml was dissolved in the appropriate volume of buffer solution. By diluting this solution with buffer solutions, solutions with the following concentrations were prepared: 0.50; 1.00; 1.50; 2.00; 2.50, and 3.00 γ Hg^{2+}/ml.

Reaction Conditions. Alekseev [1] carried out the color reaction at pH 7. We chose a pH of 4 (buffer solution) since at this pH absorption of the reaction products is a maximum. Absorption decreases with time, but measurements carried out after 5 minutes gave good reproducibility. The optical density was measured at 550 mμ; at this wavelength interference from excess reagent is a minimum (Fig. 1).

In order to establish the necessary amount of reagent, 10 ml of buffer solution containing from 0.5 to 3.0 γ Hg^{2+}/ml was taken, and 0.1 and 0.2 ml of diphenylcarbazone solution added. Higher values were obtained for the optical density on using 0.2 ml of reagent (Fig. 2). Beer's law held up to concentrations of 3.0 γ Hg^{2+}/ml. Addition of a large volume of reagent led to coagulation. Temperature variations within the limits of 15-25° had no effect on the optical density.

Experimental Procedure. By means of a pipet, 5 ml of a buffer solution containing 3.00 γ Hg^{2+}/ ml was introduced into the inner cell of the Conway diffusion apparatus, while 5 ml of a solution containing from 0.30 to 3.5 γ of CN^- was introduced into the outer cell. The apparatus was then sealed. 1 ml of the saturated tartaric acid solution was then taken up in a pipet, and the lid of the apparatus shifted horizontally so that an opening was formed over the outer cell sufficient to introduce the tip of the pipet; the tartaric acid solution was then rapidly introduced into the cell. The lid was then replaced and the solutions transferred into the outer cell by gently rocking the apparatus. It was then allowed to stand long enough for absorption to take place (4 hours at a room temperature of 20°). The lid was then removed. 0.1 ml of diphenylcarbazone solution was pipetted into the inner cell and the solution mixed with a glass rod. The solution was then transferred by means of a pipet into the spectrophotometer cell and the light absorption measured at 550 mμ 5 minutes after the color had developed. The blank solution used was a buffer solution to which reagent had been added.

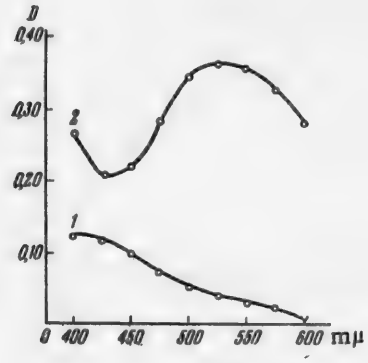

Fig. 1

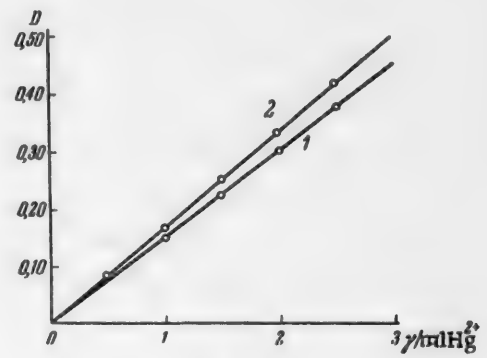

Fig. 2

Fig. 1. Absorption curves: 1) buffer solution not containing divalent mercury but containing 0.2 ml of reagent per 10 ml of solution; 2) buffer solution containing 2γ Hg^{2+}/ml and 0.2 ml of reagent per 10 ml solution.

Fig. 2. Absorption curves illustrating the effect of excess reagent: 1) on addition of 0.1 ml of reagent; 2) on addition of 0.2 ml of reagent.

A standard curve was prepared in the same way using solutions of potassium cyanide containing from 0.3 to 3.5 γ CN^-. This curve was a straight line. The standard curve can be constructed directly as well (without the microdiffusion stage).

Determination of Cyanide

CN^- taken, γ / 5 ml	CN^- found, γ/ 5 ml
0,30	0,300; 0,308; 0,292; 0,300; 0,300
0,50	0,508; 0,500; 0,492; 0,500; 0,492;
1,00	1,008; 1,000; 1,012; 1,002; 0,998
2,00	2,000; 2,008; 2,000; 1,992; 2,000
3,00	3,008; 3,000; 3,000; 2,992; 3,008
3,50	3,516; 3,500; 3,492; 3,484; 3,508

The table contains results obtained during the determination of various amounts of cyanide. Interference from sulfide ions can be eliminated by precipitation with cadmium nitrate [2].

SUMMARY

An absorptiometric method for the indirect determination of cyanide based on the color reaction of mercuric ions with diphenylcarbazone has been developed. Hydrogen cyanide is liberated by microdiffusion and is absorbed by a mercuric chloride solution. Only excess mercuric ions which have not been complexed by the cyanide is able to react with the diphenylcarbazone.

The method permits determination of 0.30-3.50 γ CN^-/ 5 ml. Separation of the cyanide by microdiffusion facilitates control of the acidity of the medium prior to carrying out the color reaction, and so eliminates the effect of foreign salts and prevents interference from halide and thiocyanate ions. Interference from sulfide ions can be prevented by precipitation with cadmium nitrate.

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PHOTOMETRIC DETERMINATION OF MICROAMOUNTS OF THORIUM

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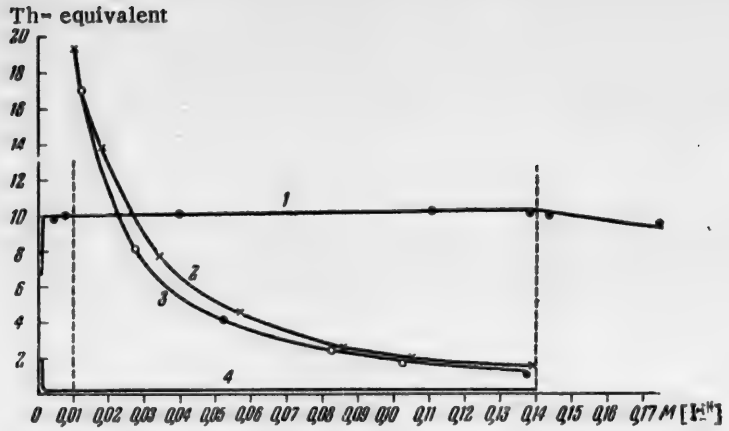
Among the reagents suggested for the photometric determination of micro amounts of thorium, the one which has found the widest application is thoron which was suggested by Kuznetsov [1, 2] and was first used for this purpose by Thomason, Perry, and Byerly [3]. During the analysis of samples containing microgram amounts of thorium, serious attention must be given to the concentration of the thorium and to its separation from elements which interfere with its determination. Of the methods used for concentrating micro amounts of thorium the most widely used ones are those based on coprecipitation of thorium with the hydroxides of iron [4-7] and aluminum [8-10]. An interesting method of concentrating thorium from natural water has been suggested by Taylor and Dillon [11], who coprecipitated thorium with calcium oxalate from 1.5 liters of water acidified with HCl. However, they did not study the completeness of coprecipitation of thorium with the precipitate of CaC_2O_4, so that to talk about the practical suitability of this method for concentrations purposes is out of the question. For removing thorium from elements which are precipitated at the same time as it on $Fe(OH)_3$, and which interfere with its photometric determination, several chromatographic [12-13], and extraction [7, 14-18] methods have been suggested. Of the methods based on coprecipitation of thorium with carriers, the most well known are the fluoride [7, 19-20] and oxalate methods [6, 19, 21]. Cerium or lanthanum are used as carriers. But, since these elements interfere with the photometric determination of thorium, them in some cases it is more expedient to precipitate thorium on calcium oxalate. Unfortunately, there is very little data available on this problem [9,11].

A number of papers have been devoted to the determination of thorium in several natural and synthetic samples, in monazite [15, 22], zircon, cassiterite, and other minerals [16], and in magnesium alloys [23]. In the work described in these papers all the operations of separating thorium from interfering elements were carried out with macro amounts of thorium (1-5 mg), and only in the last stage of the photometric determination was an aliquot part containing 20-100 γ Th taken.

In the work of Goldberg and Piccioto [7] and that of Tilton, Aldrich, and Inghram [6], the yield of thorium was controlled by means of the indicator UX_1. In these cases thorium was precipitated on LaF_3 or $La_2(C_2O_4)_3$, and then separated from the carrier by means of extraction.

In a paper by Taylor and Dillon [11] devoted to the development of a method for the determination of thorium in water thorium was precipitated with calcium oxalate directly from the total volume of test water. The precipitate of oxalates was calcined, dissolved in hydrochloric acid, and then the thorium determined photometrically. The amount of thorium in samples has been determined by the so called spike method. This method is fairly accurate as long as the requisite conditions are followed, but it increases the difficulty of determination. Furthermore, it is only applicable in those cases where the percentage precipitation of thorium on calcium oxalate in two samples is exactly the same (independently of the absolute extent of the percentage coprecipitation). However, completeness of coprecipitation was not established, and the possibility is not excluded that it is variable. Most methods have been developed for the determination of 20-100 γ of thorium; accordingly, such methods cannot be used for determining smaller amounts of thorium (of the order of 1-10 γ) without preliminary experimental checking.

In this connection we have developed a method for determining γ amounts of thorium which takes into account the possible presence of the alkali and alkaline-earth metals, U, Fe, and the rare-earths.



Relation between the extent of the absorption of solutions containing Th, Ce, La, and thoron, and the acidity of the hydrochloric acid solution 1) 10 γ Th; 2) 2 000 γ Ce; 3) 2 000 γ La; 4) thoron solution (about 0.003 %).

The reagents used (chemically pure grade), as a rule, were not given a supplementary purification, since their thorium content was below the limit at which it could be detected photometrically. The solutions were prepared from ordinary distilled water, and, after preparation, were acidified to a pH of about 1.

Thorium was determined on the basis of calibration curves. The optical density of the solutions was measured on a FÉK-M photocolorimeter (green-light filter). In order to increase the reliability and accuracy, measurements were made in one cell, i. e., the total absorption of the solution and cell was determined with respect to air. During measurements of the optical density by this method it is easy to achieve good reproducibility for the scale deflections (the error amounts to 0.001-0.002 on the optical density scale), we were unable to obtain such reproducibility when using three cells (the error in the readings amounted to 0.01).

An increase of 1 γ in the amount of thorium in solution gave an increase of 0.010 in the optical density (E) under the conditions used for carrying out the photometric reactions.

The requisite amount of thoron, in the form of a solution, was introduced into a specially prepared, accurately graduated measuring cylinder, the solution containing thorium was then added and the volume made up to 15 ml by adding acid of the requisite concentration. After mixing, the solution was transferred to the cell and its optical density measured several times (it was shown in separate experiments that equilibrium is reached in solution during the time the solution is being prepared.).

Conditions for Carrying out the Colorimetric Reaction.

Optimum Thoron Concentration. According to published results, the optimum concentration of thoron in the solution being measured photometrically is 0.01% for a wide range of thorium concentrations. According to our experiments, for work under the conditions we adopted, this concentration should be lowered to 0.002-0.003% for the determination of 1-20 γ of thorium. At a concentration of 0.004% of thoron an appreciable deviation from Beer's law occurs. For all our determinations the thoron concentration was 0.003% (more accurately 0.0029%).

The Effect of Acidity on the Absorption of the Complexes of Thoron with Thorium, Cerium, and Lanthanum.

There is a large divergence of opinion in the published literature on the optimum pH to be used. Accordingly, we studied the relation between the light absorption of solutions of the complex and the hydrochloric acid concentration. The results obtained for a complex containing 10 γ of Th, and also the values for the absorption of solutions (in units of the equivalent of thorium) containing 2000 γ Ce and 2000 γ La, and of solutions containing

TABLE 1

Effect of Calcium on the Absorption of Solutions Containing Various Amounts of Thorium

Taken		Found	Taken		Found
Ca, mg	Th, γ	Th, γ	Ca, mg	Th, γ	Th, γ
5	0	0	25	0	0,2
	10,0	10,0		5,0	5 3
	20,0	20,0		20,0	20,0
10	0	0	50	0	0,7
	1,0	1,0		2,0	2,5
	10,0	10,1		10,0	9,9
	20,0	20,1	100	0	1,3
				10,0	9,0

only thoron, as a function of the acidity is shown in the diagram. It is clear from these results that the light absorption of solutions containing only thorium remains constant on changing the pH from 2.3 to 0.85. Outside this pH range there is considerable weakening of the color. Since interference from the rare-earths, and possibly from other ions, increases with increasing pH, the acidity of the solution should be as high as possible. In our work the acidity of the solutions being measured photometrically varied from 0.11 to 0.14 N (pH 0.96-0.85).

Effect of Calcium Ions on Thorium Determination.

In order to establish the possibility of determining thorium in the presence of calcium, the effect of various amounts of calcium on the absorption of solutions containing thorium (Table 1) was studied.

From these results it is possible to draw the conclusion, which is important from a practical viewpoint, that small amounts of calcium (5-10 mg) do not cause any distortion of the results during determination of 0-20γ and more of thorium.

Coprecipitation of Thorium with Ferric Hydroxide.

Coprecipitation of thorium with Fe $(OH)_3$ was adopted for separating it from Na, K, Ca, Ba, and other metals, and for simultaneously concentrating it. Experiments carried out to establish the completeness of precipitation of thorium showed that 10^{-6} - 1000 γ of thorium can be quantitatively coprecipitated with $Fe(OH)_3$. The yield, which was determined by means of the indicators UX_1 and RdTh, varied around 100 %, only rarely dropping down to 95 %.

Preparation of a Solution of UX_1 Indicator.

In order to prepare a solution of the indicator almost free from U, Fe, and other metals we adopted the following method for separating UX_1 from $UO_2(NO_3)_2$. A concentrated solution of $UO_2(NO_3)_2$ which was 1N with respect to HNO_3 and was saturated with NH_4NO_3 was shaken 6-7 times with ether. The aqueous layer was transferred to a porcelain beaker and the solution evaporated to dryness, the residue was then slightly calcined to remove ammonium salts. The calcined residue was dissolved in concentrated HNO_3 and the solution transferred to a 50 ml beaker in which it was evaporated to dryness on a water bath. The residue was dissolved on boiling in 10 ml of water and 10 ml of a 10% solution of $H_2C_2O_4$, to this solution 10 mg of Ca^{2+} was added. When no precipitate separated out another 5 mg of Ca^{2+} was added. After 6-12 hours the precipitate was filtered off (centrifuged) and washed several times with a 1% solution of oxalic acid, it was finally washed once with water and calcined for 60 minutes at 600°. The calcium oxide obtained was dissolved in a few ml of 3.6% (1: 10) HCl, and the solution filtered through a Schott No. 4 filter and diluted to about 100 ml with 0.1 N HCl. The yield of UX_1 obtained as a result of the operations described above varied within the limits of 60-90%. The indicator solution prepared from the UX_1 purified in this way was almost free from carrier and contained traces of uranium which does not interfere with the photometric determination of thorium. 1-2 ml of this solution with an activity of 1500-2000 impulses / minute was taken for each analysis.

TABLE 2

The Relation between Completeness of Coprecipitation of Thorium with Calcium Oxalate and Various Precipitation Conditions

Taken			Acid concentration	Ca introduced	Ppt. contact time	UX_1 found in the filtrate, (%)
Th, γ	Ca, mg	other elements				
20	1,25	—	0	Before addition of $H_2C_2O_4$	12 Hours	5,8
10	5	—	0	» » »	12 »	1,6
10	5	—	0	Into the hot oxalic acid solution	12 »	0,5
10	5	—	0,15 *N* HCl	Before addition of $H_2C_2O_4$	12 »	3,7
10	5	—	0,15 » »	Into the hot oxalic acid solution	12 »	0,5
20	10	—	0,15 » »	Before addition of $H_2C_2O_4$	15 Days	16,4
20	10	—	0,15 » »	Into the hot oxalic acid solution	15 »	10,1
20	10	Fe 10mg	1,5 *N* CH_3COOH	Ditto	12 Hours	0,2
10	10	U 780 γ	0	» »	12 »	0,6
2	10	Fe 10mg U 2100 γ	Ce 50 γ	» »	12 »	1,1

Separation of Thorium from Iron and Uranium by Precipitation on Calcium Oxalate.

For removing thorium from U, Fe, and other metals which form soluble compounds with the oxalate ion, we developed a method for coprecipitating thorium with calcium oxalate from small volumes of weakly acid solutions. The procedure adopted was as follows. To the solution containing Th, U, Fe, etc. was added a known amount of indicator, and the solution evaporated to dryness in a 25-50 ml beaker on a water bath, (in the general scheme of analysis this solution is obtained on dissolving the $Fe(OH)_3$ in 3.6% hydrochloric acid), the residue was dissolved in a small amount of dilute hydrochloric acid and a few ml of water and 10% $H_2C_2O_4$ solution added, 5-10 mg of Ca^{2+} was finally added to the hot solution. After several hours the precipitate of calcium oxalate was removed from the solution by centrifuging, calcined at a definite temperature, and dissolved in a known amount of HCl; this solution was filtered through a Schott No. 4 filter and was used for the photometric determination, after which the yield of UX_1 was established.

Study of the Completeness of Coprecipitation of Thorium with Calcium Oxalate under Various Conditions.

The experiments carried out to establish the extent of the coprecipitation of thorium with calcium oxalate were carried out in the same way as that described for the general scheme of analysis; completeness of coprecipitation of thorium was determined by measuring the amount of UX_1 remaining in solution after filtering and washing the oxalate precipitate.

Preliminary experiments showed that the extent to which thorium is coprecipitated with calcium oxalate is independent (within the limits studied) of the volume of solution from which precipitation is carried out, and of the amount of $H_2C_2O_4$. In these experiments the volume was varied from 6 to 20 ml, while the relative amount of $H_2C_2O_4$ was varied from 20 to 60% (ml of 10% solution). Accordingly, in our subsequent experiments we chose the most convenient volume from a practical viewpoint, namely 9-11 ml, the oxalic acid content if which corresponded to 4 ml of a 10% solution of $H_2C_2O_4$.

It was established that it is quite satisfactory to wash the precipitate twice with a dilute solution of oxalic acid (25 g/liter), and once with water, 5 ml portions being used each time. Washing was carried out with cold solutions.

The relation between the completeness of precipitation of thorium on calcium oxalate was studied as a function of: the acidity of the solution, the amounts of calcium and thorium, the order of mixing the solutions of calcium chloride and oxalic acid, the presence of Fe, U and Ce in solution, and the time elapsed from the moment of precipitation to the removal of the precipitate from solution. The most characteristic results of these experiments are given in Table 2.

From the adduced results it is clear that completeness of coprecipitation with CaC_2O_4 is almost independent of the amount of Th and Ca in solution, apart from the smallest amount of calcium taken (1.25 mg) when the loss of thorium amounts to 6%. It is obvious that 10 mg of carrier is completely sufficient for almost complete quantitative separation of 1-20 γ of Th from solution.

Changes in the acidity of the solution from 0 to 0.15 N with respect to HCl also have no effect on completeness of precipitation of thorium. But, since at an acidity of 0.15 N, calcium oxalate is precipitated with great difficulty, we chose an acidity of about 0.04 N with respect to HCl.

In certain cases coprecipitation of thorium with CaC_2O_4 from concentrated acetic acid solution may be interest.

The presence of the foreign ions studied in solution has little effect on the completeness of coprecipitation of thorium. Completeness of coprecipitation of thorium depends to a somewhat greater extent on the order of mixing of solutions of $CaCl_2$ and $H_2C_2O_4$, and the time for which the precipitate is allowed to stand in contact with the solution; this can be explained by the absorption mechanism of the coprecipitation of thorium with CaC_2O_4. On adding the carrier to hot oxalic solutions, the CaC_2O_4 precipitate formed traps thorium better than during precipitation from calcium-containing solutions to which oxalic acid is added. Obviously, in the first instance finer crystals with a larger surface are formed which strongly absorb thorium. On standing, the crystals of calcium oxalate get larger, their surface decreases, and completeness of coprecipitation of thorium with them decreases.

In practice the precipitate of calcium oxalate settles out completely in a few hours, and in our method is separated from solution by centrifuging 6-12 hours after precipitation.

Conditions for Treating the Precipitate of Calcium Oxalate

In order to remove the calcium oxalate precipitates from solution we adopted centrifuging instead of filtration which is more practical and convenient, since we did not wish to introduce any additional contamination into the solution. We found that filter paper ash sometimes led to considerably turbidity of the solution, and that certain ashless filter papers (particularly blue band) contain an appreciable amount of iron.

Centrifuging was carried out at 2000 revolutions/minute in 15 ml quartz tubes. 0.5-1 ml of alcohol was poured onto the aqueous layer before centrifuging otherwise a film of the precipitate remained on the water surface. After centrifuging and washing, the precipitate of CaC_2O_4 was calcined at 600-650° for 60 minutes. It was found that precipitates calcined at a lower temperature gave turbid solutions when the residue was dissolved. Precipitates calcined at a higher temperature were more difficult to dissolve in hydrochloric acid, leading therefore to an increase in thorium loss. The CaO residues obtained were dissolved in 1 ml of 3.6% HCl on boiling (the residue dissolved without heating after 1-2 hours). The solutions obtained in this way always contained some mechanical impurities (dust falling in at various stages; particles formed during calcination of the oxalate; SiO_2 which often gets into these solutions during the analysis of mineral samples) so that these solution had to be filtered through No. 4 small-size Schott filters. Not more than 5% of thorium was lost on the filter during this stage, and the solutions obtained were, as a rule, completely clear. The filtrate was collected in a small beaker, and the filter washed 2-3 times with 0.1 N HCl, the washings being collected in the same beaker until the total volume was 10-12 ml. The solution was then transferred to a measuring cylinder, the thoron solution was added and the solution measured photometrically. After the absorption had been measured the solution was transferred to a 40 ml cell and its β-activity measured on an AS-2 counter.

Analysis of Synthetic Samples. In order to check the method developed, a large number of synthetic samples containing various amounts of thorium and various interfering elements were analyzed. Results of these experiments are given in Table 3.

It is clear from these results that in some cases the results are somewhat high, obviously because of the thorium content of the indicator solution. The extent of this increase, which was carefully determined after preparing each new indicator solution, was taken into account during calculation of the results for the analysis of Th-containing materials.

The mean absolute error during determination of thorium in synthetic and other samples varied around 0.3 γ Th. The maximum absolute error was taken to be 0.5 γ.

TABLE 3

Determination of Thorium in Synthetic Samples

Taken		Yield of UX_1	Th found	Error	Taken		Yield of UX_1	Th found	Error
Th, γ	other elements, mg	%	γ		Th, γ	other elements mg	%	γ	
0	—	—	0,1	+0,1	10	—	99	9,5	—0,5
0	Fe^{3+} 10	—	0,2	+0,2	25	—	94	24,8	—0,2
0	Fe^{3+} 10; 2	—	0,3	+0,3	10	U 17	96	10,3	+0,3
0	—	96	0,2	+0,2	10	Fe^{3+} 10	95	9,5	—0,5
2	—	92	1,9	—0,1	5	Fe^{3+} 10; U 2	95	4,8	—0,2
5	—	96	5,2	+0,2	15	Fe^{3+} 10; U 2	96	15,2	+0,2

Note. 10 mg of Ca was used for coprecipitating the Th.

TABLE 4

Determination of Thorium in the Presence of Cerium

Taken		Q_1	Q_2*	H^*_1	H_2*	Th found, γ	Error, γ
Th, γ	Ce, γ						
10	2000	11,0	14,0	0,140	0,023	10,5	+0,5
10	2000	11,2	15,0	0,143	0,027	10,5	+0,5
10	6000	10,2	15,4	0,159	0,027	10,1	+0,1
10	6000	9,5	15,2	0,159	0,025	9,5	—0,5

* H_1 and H_2 are the initial and final acidities of the solution being measured photometrically; Q_1 and Q_2 are the amounts of thorium corresponding to the optical density of the solution found at the initial and final acidity.

During accurate and careful work, the observed deviations of the results obtained from the true values rarely exceeded the value of the maximum absolute error. This accuracy is quite permissible for the determination of 2-10 γ and more of thorium. During the determination of smaller amounts of thorium it is necessary to take special precautions in order to decrease the value of this error.

Determination of Thorium in the Presence of the Rare-Earths.

When the method described is used for the separation of thorium from certain interfering elements, the rare-earths are precipitated together with thorium on the calcium oxalate, and, since the rare-earths interfere with the photometric determination of thorium, it becomes necessary to separate them or to make the necessary correction. We attempted to develop a method for determining this correction; for this purpose use was made of the different relationships between the absorption of the complexes formed by thoron with thorium and the rare-earths and the pH value of the solution. It is clear from the diagram that while the absorption of solutions containing thoron and 10 γ of thorium remain constant on changing the acidity of the solution from 0.005 to 0.14 N, the absorption of solutions containing 2000 γ Ce or La increases with decreasing acidity, within the limits indicated, by 19:1.3 = 14.6 times. Accordingly, by measuring the absorption of solutions containing thorium and cerium (lanthanum) at two different pH's, and knowing how the absorption caused by Ce (La) varied during this change in acidity, it is possible to calculate the value of this absorption, so that an appropriate correction can be applied.

Using such a technique it is possible to determine thorium quantitatively in the presence of an unknown amount of the rare-earths, as long as the character of the relationship between the absorption of the complexes of the individual rare-earths with thoron and the acidity of the solution is the same, independently of the absolute value of the absorption of the individual complexes. Unfortunately, we were only able to study cerium and lanthanum in this connection. Nevertheless, in our opinion, this method could be used for the determination of thorium in the presence of a natural mixture of the rare-earths, since, in the first instance Ce and La account for

the bulk of the elements in a natural mixture of the lanthanides, and in the second place one would not expect a sharp difference in the relationship indicated for the remaining rare-earths from that for Ce and La, although, of course, during such a determination a certain indeterminacy always exists. Table 4 contains some results for the determination of thorium in the presence of various amounts of carium by the method indicated.

During the determination of 10γ or more of thorium, the increase over true value caused by the presence of 1-2 mg of the rare-earths can be ignored in practice, if the acidity of the solution being measured photometrically is maintained equal to 0.14 N. In order to get more accurate results a correction should be applied, the value of the correction being ascertained by the method suggested. This method, of course, cannot yield a high accuracy when it is used as a method for separating thorium and the rare-earths, but it may be useful for getting an approximate idea of the increase over the true value caused by these elements during mass analyses.

SUMMARY

Optimum conditions have been established for the photometric determination of thorium by means of thoron when the optical density of the solutions is measured on the FÉK-M photocolorimeter.

A method has been developed for separating microgram amounts of thorium from uranium, iron, and other interfering elements, which is based on coprecipitation of thorium with calcium oxalate from a weakly acid medium.

A method is proposed for the determination of thorium in the presence of cerium and lanthanum; this is based on differences in the absorption of the colored complexes of these elements with thoron at various acidities of the solution. The mean absolute error for the determination of 1-10 γ of thorium is 0.3 γ. The maximum absolute error does not exceed 0.5γ.

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 5. THE PHOTOMETRIC DETERMINATION OF MOLYBDENUM

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The most widely used photometric method for the determination of molybdenum is the thiocyanate method [1,2]. The fairly large instability constant of the thiocyanate complex makes it essential to add a large excess of ammonium thiocyanate, and this leads to the partial formation of the somewhat less intensely colored complex ion $[Mo(SCN)_6]$. During careless reduction of molybdenum to the quinquevalent state there may be formed molybdenum compounds in which the molybdenum is in the lower valence states and these compounds will be less intensely colored. Extracts of molybdenum thiocyanate in organic solvents have low stability. Fe, Co, Ni, Al, Ti, Mn, U, and Ta do not interfere with determination of molybdenum by this method. The platinum metals, silver, gold, and a number of other elements should be absent. This method can be used for the determination of molybdenum in tungsten salts under conditions where iron is absent. Phenylhydrazine [2] and potassium ethylxanthate [3] give a fairly sensitive reaction with molybdenum in acid media.

The phenylhydrazine reaction is used for the determination of molybdenum in ores and silicate rocks [4,5].

In addition to the reagents mentioned above, several sensitive reagents, which, however, are of low specificity have been suggested for determination of molybdenum; these include thioglycollic acid [6], and protocatechaldehyde [7]. Dithiol (4-methyl-1,2-dimercaptobenzene) has started to find use in recent years for the determination of molybdenum in soils and plants. This reagent requires preliminary separation of molybdenum from accompanying elements.

Another drawback of this reagent is its low stability; despite this, because of its high sensitivity, dithiol is finding application for the determination of small amounts of molybdenum (about 0.1 γ) [8-10].

Thiooxine (the sulfur-containing analog of 8-hydroxyquinoline) reacts with molybdates both in weakly and in strongly acid solutions to form insoluble compounds. Depending on the conditions, various molybdenum thiooxinates can be obtained. At pH 2-3, and also in more acid media, ammonium molybdate reacts with thiooxine to form an amorphous brown precipitate, which, in the presence of excess thiooxine becomes green. The green thiooxinate has the composition $MoO_2(C_9H_6NS)_2 \cdot H_2O$.

Found %: Mo 20.64; N 6.29; S 13.67; H_2O 3.82
Calculated %: Mo 20.59; N 6.01; S 13.30; H_2O 3.86

The water of crystallization in the molybdenum complex was determined by two methods: by drying, and by the Chugaev-Zerewitinoff method for the determination of active hydrogen [11]. Both methods gave identical results.

This molybdenum thiooxinate is readily extracted by chloroform, isoamyl alcohol, toluene, xylene, benzene and bromobenzene to give emerald-green colored solutions; it is sparingly soluble in carbon tetrachloride and dichloroethane. It is completely insoluble in aliphatic hydrocarbons. The extracts maintain a constant extinction for at least 24 hours.

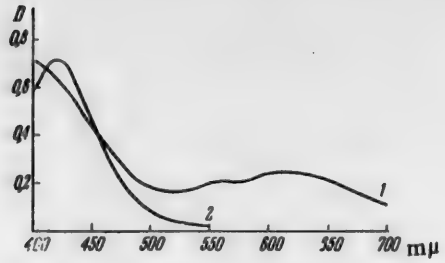

Fig. 1. Absorption curves for molybdenum thiooxinate. 1) Without ascorbic acid; 2) in the presence of ascorbic acid.

At higher acidities thiooxinates of different composition may be formed. In a 1:1 hydrochloric acid solution, there is formed a brown amorphous precipitate containing 16.46 % Mo, 18.14% S, 4.95% N, and 3.54% H_2O. This complex is extracted by chloroform to give a solution with a brown color.

From concentrated hydrochloric acid green crystals are precipitated which contain: 14.80% Mo, 27.14% S, 4.27% N, and 7.29% H_2O.

In weakly acid solutions (pH 3-5), in the presence of ascorbic acid, presumably, there occurs reduction of the molybdenum to the quinquevalent state, since the molybdenum thiooxinate extracted afterwards from 2.3 N HCl has a yellow color. The extractability by organic solvents, and the stability of the extracts of this complex are the same as those for $MoO_2(C_9H_6NS)\cdot H_2O$ mentioned above.

The absorption curves for molybdenum thiooxinates are shown in Fig. 1.

As is evident from Fig. 1, the absorption maximum of the molybdenum thiooxinate extracted by toluene in the presence of ascorbic acid is shifted to long wavelength side of the spectrum, and is found at 420 mμ. The molar extinction coefficient $\epsilon_{420} = 8600$.

All the experiments described below were carried out with the molybdenum thioxinate obtained in the presence of ascorbic acid.

For studying the extractability of the molybdenum thiooxinate as a function of the acidity of the medium, 50 γ of Mo in the form of an aqueous solution (5 ml), and 5 ml of a 10 % ascorbic acid solution were introduced into a separating funnel and left to stand for 2-3 minutes. Then, in the case of high acidities, the calculated amount of hydrochloric acid was added, while in the case of weakly acid solutions a buffer solution with a definite pH was added, until the volume was 50 ml. After addition of 4 ml of 4-5% alcoholic solution of thiooxinedihydrate or thiooxine hydrochloride (in 2.3 N HCl for strongly acid solutions) the molybdenum thiooxinate was extracted with 10 ml of toluene by vigorous shaking for 5 minutes. The extract was filtered through a plug of cotton wool and photometric measurements carried out; the amount of molybdenum was then calculated on the basis of a calibration curve constructed in weakly acid solutions. Since determination of molybdenum in the presence of foreign elements was carried out in a medium of 2.3 N HCl in the presence of oxalic acid (for preventing precipitation of tungstic acid), it was very important to establish the highest acid concentration at which complete extraction of molybdenum thiooxinate could still be carried out. For this purpose 20 ml of a saturated solution of oxalic acid was added to the funnel in addition to the hydrochloric acid. The acidity arising from the presence of the oxalic acid was not taken into account.

As can be seen from Fig. 2, molybdenum thiooxinate can be completely extracted within the limits of pH 5 to 2.3 N HCl; in more acid solutions the extractability of molybdenum thiooxinate gradually drops. In alkaline solutions the molybdate does not react with thiooxine; obviously, under these conditions the molybdate is more stable than the thiooxinate.

Conformation of solutions of the molybdenum complex to Beer's law was studied under the same conditions as those that were use in subsequent work, i. e. in a medium of 2.3N HCl in the presence of ascorbic acid (5 ml of a 10% solution), oxalic acid (20 ml of a saturated solution) and 4 ml of a 5% solution of thiooxine hydrochloride in 2.5 N HCl. The only variable in all the experiments was the amount of molybdenum (from 10 to 250 γ in a volume of 50 ml). As can be seen from Fig. 3, molybdenum thiooxinate solutions conform to Beer's law down to concentrations of 10 γ Mo in 1 ml of toluene. Above this molybdenum concentration there is deviation from linearity; this fact, however, does not preclude the use of this part of the calibration curve for photometric determinations. The method permits the determination of as little as 5γ of Mo in 50 ml of test solution. When an SF-4 spectrophotometer is used and the volume of extract is 5 ml the lower limit is 1.5 γ Mo.

Even very high concentrations of most anions do not interfere with molybdenum determination; thus fluoride, bromide, sulfate, chloride, phosphate, and acetate do not interfere. Several milligrams of thiocyanate in a volume of 50 ml of test solution mask μ gram amounts of molybdenum. Nitrates apparently do not interfere with

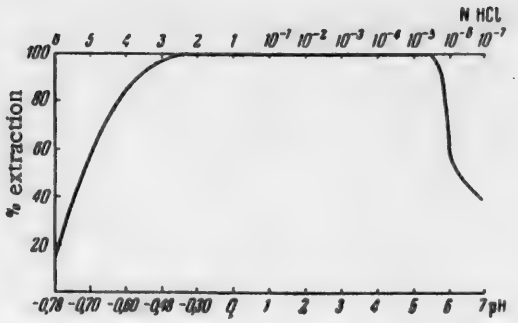

Fig. 2. The relationship between the extractability of molybdenum thiooxinate and the acidity of the solution .

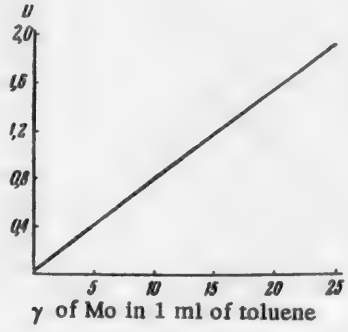

Fig. 3. Conformity of solutions of molybdenum thiooxinate in toluene to Beer's law .

molybdenum determination, but large concentrations of nitrates in a medium of 2.3 N HCl exhibit an oxidizing action on the reagent; this may be the reason for the low results obtained during determination of molybdenum. Oxalates (20 ml of saturated solution) modify the shape of the calibration curve in the region of high molybdenum concentrations.

Thiooxine, as a reagent which contains the sulfhydryl group, does not react with elements which do not form sulfides which are stable to the action of water. As a consequence of this, high concentrations of the alkali, alkaline-earth metals, Ti, Zr, Cr, Al, etc., do not interfere with molybdenum determination.

The specificity of the thiooxine method depends on the conditions used for carrying out the reaction, and depends in the first instance on the acidity of the medium. In 2.3 N HCl amounts of Fe, Co, Ni, Zn, Cd, Pb, Mn, U, Tl, Ir, Rh which are in considerable excess of the molybdenum have no effect on the accuracy of molybdenum determination. Bi, Ag, Au, Hg, and W under these conditions form thiooxinates which are insoluble in toluene or xylene. The bulky amorphous precipitates of their thiooxinates interfere with the separation of the extract, as a result of which the elements indicated should be masked. Os, Ru, Cu, Pt, and Pd interact with thiooxine in strongly acid solutions and should be masked. Thiourea is used for masking Os, Ru, Pt, Ag, Au, Bi, Hg, and Cu. The thiourea complexes of these elements are readily soluble in water and are more stable than the thiooxinates in the presence of excess thiourea in 2.3 N HCl. Palladium should not be present in amounts greater than 50γ. Tungstic acid is kept in solution by means of oxalic acid. Iron must be reduced to the divalent state with ascorbic acid, while vanadium should be reduced to vanadyl.

Determination of Molybdenum

Preparation of Reagent Solution. 5 g of the potassium salt or the hydrochloride of thiooxine is dissolved in 77 ml of water and 23 ml of concentrated hydrochloric acid (sp. gr. 1.18) added. The clear, orange-yellow solution obtained is stable for several weeks.

Analytical Procedure. To 15-20 ml of a weakly acid (pH 3-5) test solution in a separating funnel is added 4-5 ml of a 8% solution of thiourea and 5 ml of a 10% ascorbic acid solution. The mixture is allowed to stand for 3 minutes and then 10 ml of a sat·oxalic acid solution added, followed by 9.5 ml of concentrated hydrochloric acid (sp. gr. 1.18). Water is added to bring the volume up to 50 ml and the whole thoroughly mixed; 3 ml of reagent solution is then added dropwise and with stirring. Molybdenum thiooxinate is extracted by vigorous shaking with 10 ml of xylene or toluene for 5 minutes. The extract is filtered through a plug of cotton wool and the light absorption of the filtrate determined; the amount of molybdenum is determined on the basis of a calibration curve constructed with the aid of pure solutions of molybdenum, using all the reagents mentioned above. Table 1 contains results for the determination of molybdenum in the presence of foreign elements.

Table 2 contains results for the determination of molybdenum in synthetic mixtures.

SUMMARY

Thiooxine reacts with molybdenum to form an inner-complex salt with the composition $MoO_2(C_9H_6NS)_2 \cdot H_2O$. In the presence of excess thiooxine, the molybdenum complexes are stable in strongly acid solutions and are readily extracted by many organic solvents.

TABLE 1

Determination of Molybdenum in the Presence of Foreign Elements (50 γ Mo taken)

Foreign element, mg	Ratio Mo : element	Mo found, γ	Foreign element, mg	Ratio Mo : element	Mo found γ	Foreign element mg	Ratio Mo : element	Mo found γ
Fe^{3+} 10	1:200	52	Bi^{3+} 25	1:500	51	Cd^{2+} 100	1:2000	50
Ni^{2+} 40	1:800	50	Au^{3+} 25	1:500	48	Zn^{2+} 10	1:200	48
Co^{2+} 5	1:100	50	Sb^{3+}—0,05	1:1	52	Os^{VII} 0,5	1:10	51
W^{VI} 50	1:1000	52	Pt^{IV} 5	1:100	51	Ru^{VIII} 0,5	1:10	47
V^{IV} 50	1:1000	51	Ag^{+} 20	1:400	47	UO^{2+} 50	1:1000	49
Cu^{2+} 5	1:100	52	Pt^{2+} 20	1:400	48	Mn^{2+} 100	1:2000	50
Hg^{2+} 50	1:1000	48	Pd^{2+} 0,05	1:1	52	Tl^{+} 50	1:1000	50

TABLE 2

Determination of Molybdenum in Synthetic Mixtures (50 γ Mo taken)

Foreign elements taken, mg	Mo found γ	Error, %
Fe^{3+} 10; Ni^{2+} 10; Co^{2+} 10; Mn^{2+} 56	49	—2
Fe^{3+} 10; Ni^{2+} 10; Zn^{2+} 5 Ti^{IV} 10; Zr^{IV} 20; V^{V} 5	52	+4
Cr^{3+} 20; Mn^{2+} 10; V^{V} 5 Zn^{2+} 5; Cu^{2+} 2; Pb^{2+} 10	51,5	+3
Hg^{2+} 5; Ag^{+} 5; Cu^{2+} 3 Au^{III} 5; Bi^{III} 2	48	—4
W^{VI} 30; Fe^{3+} 5; Cu^{3+} 3 Bi^{III} 2; Ti^{IV} 20; Zr^{IV} 20	52,5	+5

A method has been developed for the determination of molybdenum (1.5-200 γ) in the presence of Fe, Co, Ni, W, V, Cu, Hg, Bi, Au, Pt, Pd, Os, Ru, Pb, Ag, Zn, Cd, U, Tl, and Mn.

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TITRIMETRIC DETERMINATION OF MANGANESE AFTER ITS OXIDATION TO THE TRIVALENT STATE

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The presence of chromium and certain other elements complicates the determination of manganese by titrimetric methods based on oxidation of manganese to permanganate; titration of Mn^{2+} with a solution of a permanganate to MnO_2 is also complicated. This has led to studies of the possibility of using the oxidation of Mn^{2+} to Mn^{III} in the presence of materials forming stable complexes of trivalent manganese, e.g., ethylenediaminetetraacetic acid [1], metaphosphates [2], pyrophosphates [3], and fluorides [4-8]. In these methods it is necessary to filter excess solid oxidizing agent (lead dioxide) [1], to adopt combined oxidation of Mn^{2+} by dichromate in the presence of arsenite [2,4,5], and to resort to the potentiometric determination of the endpoint of the titration of Mn^{2+} with permanganate solution [3,6,7,8],etc .....

The present article contains a description of a simple method of determining Mn^{2+} based on the formation of fluoromanganiate.

Oxidation of Mn^{2+} to "fluoromanganiate" in the presence of excess hydrofluoric acid by the action of potassium nitrate does not proceed quantitatively either in the cold or on heating, as a consequence of the reversibility of the reaction $2Mn^{2+} + NO_3^- + 2nHF \rightleftharpoons 2MnF_n^{(n-3)-} + NO_2^- + (2n-2)H^+ + H_2O$. Actually, on adding excess nitrite to a suspension of $K_2MnF_5 \cdot H_2O$ in hydrofluoric acid, a rapid, complete reduction of the fluoromanganiate occurs. However, ammonium nitrate quantitatively oxidizes Mn^{2+} to fluoromanganiate, since ammonium ions remove nitrite ions ($NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$); excess NO_3^- does not hinder the determination of the fluoromanganiate formed.

Trivalent manganese in the presence of Fe^{III} or Cr^{III} can be determined iodometrically or by titration with Mohr's salt. Results for the determination of Mn^{III} by both methods coincide. Thus, despite the increase in the reducing properties of Fe^{2+} ions in the presence of fluorides, oxidation of Fe^{2+} ions by atmospheric oxygen during the titration does not occur to an appreciable extent; the introduction of boric acid to complex F^- ions, does not affect the results of titration with Mohr's salt. In the presence of chromium it is essential to introduce boric acid before titrating Mn^{III}, since chromium fluoromanganiate $CrF_3 \cdot MnF_3 \cdot 6H_2O$ [9] is very slowly reduced in the presence of excess hydrofluoric acid.

When manganese, iron, and chromium are present simultaneously Mn^{III} cannot be determined iodometrically since Fe^{3+} ions freed from the fluoride complex on addition of boric acid, oxidize the iodide anions.

Moderate amounts of cobalt or nickel salts do not hinder determination of manganese.

Reducing agents (SO_2 and other materials) which are usually present as impurities in hydrofluoric acid do not interfere with the determination, since they are completely oxidized during oxidation of Mn^{2+} to fluoromanganiate.

The concentrations of the standard solutions of chemically pure manganese nitrate, containing 8.47 or 15.56% Mn, were established by the bismuthate method. Aliquots of solutions were taken under conditions which excluded evaporation.

TABLE 1

Oxidation of Mn^{2+} by Nitrates in the Presence of HF

Amount of reagents			°C	Duration of oxidation, minutes	Amount of Mn		Percentage oxidation of Mn, %
40% HF, ml	KNO_3, g	HN_4NO_2, g			taken, mg	found, mg	
10	1	—	15	30	58,19	26,63	46,08
10	1	—	15	60	43,52	30,02	68,98
10	2	—	15	30	40,87	26,63	65,15
10	1	—	100	30	37,88	28,68	77,48
10	—	2	15	30	49,58	43,80	88,20
10	—	2	100	10	56,26	56,25	99,98
7	—	3	100	10	59,53	59,53	100,00
3	—	1,5	100	10	50,15	49,46	99,62
3	—	0,5	100	10	54,01	46,19	85,30

TABLE 2

Determination of Mn in the Presence of Cr^{3+}

Atomic ratio Cr/Mn in the test solution	Mn taken, mg	Mn found	
		in mg	in %
1	41,11	40,97	99,80
2	36,02	35,85	99,66
4	36,22	36 00	99,40
4	25,28	25,06	99,45
4	26,42	26,36	99,78

TABLE 3

Determination of Mn in the Presence of Fe^{3+} and Cr^{3+}

Atomic ratios in the test solution		Mn taken, mg	Mn found	
Fe/Mn	Cr/Mn		in mg	in %
1	0	21,14	21,03	99,58
4	0	25,63	25.52	99,55
4	2	27,58	27,56	99,94
4	2	29,96	29,60	98,90
4	2	32,20	31,96	99,20
4	2	33,30	33,20	99,80

In the first series of experiments potassium nitrate was the oxidizing agent, while urea was used for combining with the nitrite before titration. It was found (Table 1) that oxidation of Mn^{2+} proceeds with time, increases with increasing temperature, but does not proceed to completion. The use of not less than 1.5 g of NH_4NO_3 and 3 ml of 40% HF permits 1 mg-atom of Mn to be oxidized quantitatively on boiling for 10 minutes on a water bath. The experiments, results of which are given in Table 1, were carried out under the following conditions. To an aliquot of manganese nitrate in a platinum crucible was added hydrofluoric acid and potassium nitrate; the mixture was then kept for a given time at room temperature or on a boiling water bath. After this the mixture was diluted to 100 ml with cold water in a glass flask, and to it was added about 2 g KI, and the iodine liberated titrated with thiosulfate.

Decreasing the initial concentration of the hydrofluoric acid lowers the percentage oxidation of Mn^{2+}; during attempts to use a mixture of nitric acid and 40% hydrofluoric acid as an oxidizing agent, the percentage oxidation of Mn^{2+} dropped rapidly, apparently, because of a decrease in the active concentration of fluoride ions.

Results of the first determinations of manganese in mixtures of Mn^{2+} and Cr^{3+} salts were appreciably low. It was found that the reason for this was not a decrease in the percentage oxidation of Mn^{2+}, but the precipitation of $CrF_3 \cdot MnF_3 \cdot 6H_2O$ which is only slowly reduced by the iodide. Since keeping the solution for a long time before titration with thiosulfate would give rise to the danger of oxidation of I^- by atmospheric oxygen, we tried to accelerate dissolution of the precipitate of $CrF_3 \cdot MnF_3 \cdot 6H_2O$ by addition of boric acid; actually, after adding about 8 g of H_3BO_3 and 50 ml of 10% HCl, the precipitate was rapidly and quantitatively reduced by the iodide.

Under these conditions it is possible to determine the manganese content accurately in the presence of four times its amount of chromium. To aliquots of the solutions placed in a platinum crucible was added 7 ml of 40% HF and 2-3 g of NH_4NO_3; the solution, which was heated for 10 minutes on a boiling water bath, was then transferred into a flask and diluted with a mixture of HCl, H_3BO_3, and water; after addition of KI to this mixture the liberated iodine was titrated with thiosulfate. Results of these determinations are given in Table 2.

TABLE 4

Determination of Mn in the Presence of Co^{2+} or Ni^{2+}

Atomic ratios in the test solution		Mn taken, mg	Mn found		Atomic ratios in the test solution		Mn taken, mg	Mn found	
Co/Mn	Ni/Mn		in mg	in %	Co/Mn	Ni/Mn		in mg	in %
0,9	0	46,10	45,77	99,28	0	0,75	55,59	55,49	99,82
1,0	0	42,64	42,58	99,85	0	0,9	46,31	46,15	99,66
1,8	0	40,57	40,93	100,89	0	1,0	61,40	60,90	99,19
3,6	0	61,24	60,98	99,59	0	1,4	36,11	36,26	100,42
4,0	0	62,20	62,10	99,94	0	2,0	67,80	64,80	95,58
5,0	0	65,45	63,10	96,41	0	3,5	63,22	60,92	96,34
6,7	0	65,86	63,46	96,35	0	6,8	64,49	54,93	85,18

TABLE 5

Determination of Mn in Ferromanganese Containing 74.9% of Mn.

Weight of alloy, mg	Mn, mg	Mn found	
		in mg	in %
34,6	25,92	25,86	99,79
37,0	27,71	27,71	100,00
30,0	22,47	22,70	99,50
34,0	25,46	25,34	99,53
34,8	26,06	25,94	99,52

Mixtures containing Mn^{2+}, Cr^{3+}, and Fe^{3+} were heated with HF and NH_4NO_3 under the same conditions; the mixture was then diluted with 50 ml of 3% NH_4NO_3 containing 8 g H_3BO_3 (partly in suspension) and with water (to a volume of 200 ml); the precipitate of MnO_2 was immediately titrated with a solution of Mohr's salt in the presence of diphenylamine. Results of these determinations are given in Table 3. A further increase in the absolute content of chromium interferes with the determination of manganese, since chromium salts mask the change in color of diphenylamine.

As the results in Table 4 show, the presence of cobalt salts (up to about 250 mg) or nickel salts (up to about 70 mg), does not interfere with the determination of manganese either; under these conditions the determination was finished iodometrically.

It was found that under the conditions used, Co^{2+} salts were not oxidized to Co^{III} as might have been expected on the basis of the extremely strong oxidizing properties of fluorocobaltiates. A drop in the degree of oxidation of Mn^{2+} in the presence of large amounts of Co^{2+} and Ni^{2+} is caused, presumably, by a decrease in the concentration of F^- ions and by the increase in acidity of the solutions caused by oxidation of the fluorides, and also by the dilution of the solutions (Co^{2+} and Ni^{2+} were introduced in the form of the hydrated sulfates).

In conclusion, the applicability of the method developed for the analysis of ferromanganese (standard sample No. 35, containing 74.9% Mn) was checked. An aliquot of the ground ferromanganese, containing about 0.5 g. atom of Mn, was dissolved on heating in 15 ml of 49% HNO_3 contained in a platinum crucible. After the aliquot had dissolved completely, NH_4F in an amount equivalent to the amount of acid taken was added to the crucible; this simultaneously depressed the acidity of the solution (as a result of the replacement of HNO_3 by HF) and introduced the NH_4^+ and F^- ions necessary for the analysis. The mixture was heated for a further 10 minutes and was then transferred into a glass flask by washing with water, after which 50 ml of 3% HNO_3 was added, followed by water (to a volume of about 200 ml); the mixture was immediately titrated with a solution of Mohr's salt in the presence of diphenylamine. As the results given in Table 5 show, the accuracy of the method is fully satisfactory.

SUMMARY

Mn^{2+} ions are quantitatively oxidized to fluoromanganiate on heating them with ammonium nitrate and hydrofluoric acid. Determination of the fluoromanganiate formed can be carried out iodometrically or by titration with Mohr's salt in the presence of diphenylamine.

The presence of salts of Fe^{3+}, Cr^{3+}, Co^{2+}, and Ni^{2+} does not prevent oxidation of the Mn^{2+}.

The slow rate at which the sparingly soluble precipitate $CrF_3 \cdot MnF_3 \cdot 6H_2O$ is reduced by the action of iodide necessitates the addition of boric and hydrochloric acids; when chromium and iron are simultaneously present, the solution should be titrated with Mohr's salt.

The method suggested can be used for analysis of ferromanganese.

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FUNCTIONAL ANALYTICAL GROUPS FOR PALLADIUM

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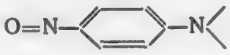
In 1930 Overholzer and Yoe [1] suggested a photometric method of determining Pd (II) by means of p-nitrosodiphenylamine. The same authors investigated a large number of reagents for palladium such as p-nitrosodiphenylamine, p-nitrosoaniline, p-nitrosodimethylaniline, and p-nitrosodiethylaniline [2]. Having studied these reagents and similar compounds, Kul'berg [3] suggested the following functional-analytical group for Pd (II):



According to Overholzer and Yoe's results compounds of the following type are formed:

The aims of our investigations were:

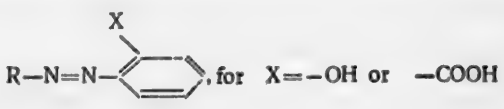
a) To find a more general functional group for Pd (II) than that suggested by Kul'berg; b) to develop sensitive photometric methods for determining palladium, including methods for its determination in the presence of platinum.

In this connection we examined 22 organic materials and came to the following conclusions:

1. The most general group is the following (see Table 1):

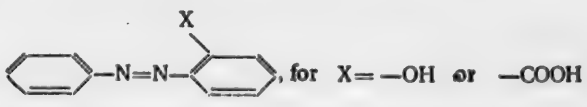
It includes the group found by Kul'berg.

2. During a study of the reactions of palladium (II) with a number of azo dyes (see Table 2) of the type:



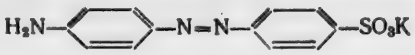
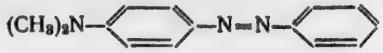
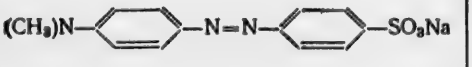
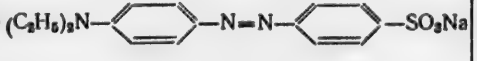
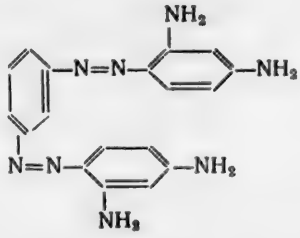
it was found that they all react with palladium.

As a result of a comparison of the formulas of the reagents studied it is possible to indicate yet another functional-analytical group with the following structure for palladium:



For the photometric determination of palladium we chose four reagents, namely: benzyl orange, methyl orange, magneson 1 and methyl red.

TABLE 1

Reagent	Formula	Color of the reagent with: CH_3COONa	Color of the reagent with: CH_3COONa and $PbCl_2$
Benzyl orange		Yellow	Yellow-brown
p-Dimethylaminoazobenzene (dimethyl yellow)		Yellow	Red-brown
Methyl orange		Yellow-orange	Brown
p-Diethylamino-azobenzene-4'-sulfonic acid sodium salt		Orange	Brown
Vesuvin		Orange	Red-brown

The maximum color developed with benzyl orange and methyl orange after 30 minutes.

The color with magneson 1 changed gradually; the optical density of the solutions was always measured after 10 minutes.

The concentration of the $PdCl_2$ solution (established by means of dimethylglyoxime) was 98.33 γ[Pd]/ml. For measurements of the optical density, the reference solution contained the same amounts of the reagents as the solution containing palladium. The pH was maintained constant by addition of sodium acetate (1 ml of a 2 % solution) to the test solution and to the reference solution. The pH used lay outside the color change range when these reagents are used as indicators (6-7.5). The total volume was 10 ml. The optical density was measured on a Pulfrich photometer with a light filter whose transmission maximum coincided approximately with the absorption maximum of the solutions; the pH was determined by means of a pH meter type P_5/P_6 No. 35 .

The results obtained are given in Table 3 and Fig. 1 .

In Fig. 2 are shown the absorption curves of the compounds of palladium with the azo dyes.

Bearing in mind that both components are colored, establishment of the stoichiometric ratios of the reagents during their interaction in solution cannot give conclusive results.

Nevertheless, indications can be obtained regarding the amounts of reagents necessary for developing the optimum color intensity. Both spectrophotometric and refractometric studies of benzyl orange and methyl orange (Tables 4-7) showed that the stoichiometric ratios are, respectively, 6 Pd: 1R and 3 PD: 1R (R = Reagent).

Thus, maximum absorption was obtained with 0.5 ml of reagent for 1 ml $PdCl_2$.

2 ml of 0.01 % benzyl orange was necessary for 393.3 γ Pd.

TABLE 2

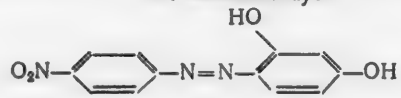
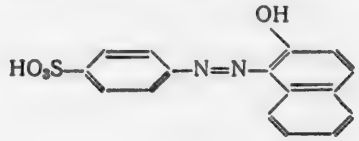
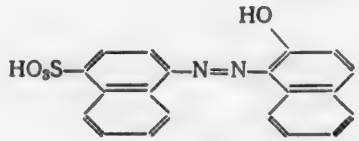
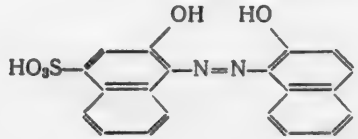
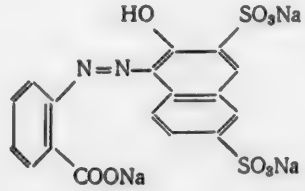
Reagent	Formula	Color of the reagent with:	
		CH_3COONa	CH_3COONa and $PdCl_2$
	A. Monoazo dye		
Magneson I		Yellow-orange	Brown
Orange II		Orange	Red-brown
Red acid A B		Red	Red-violet
Blue acid chromatin		Blue	Red-violet
Alizarin red acid B		Yellow	Orange

TABLE 2 (continuation)

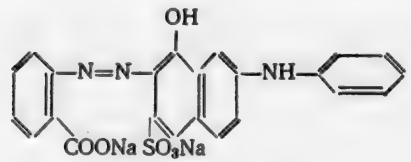
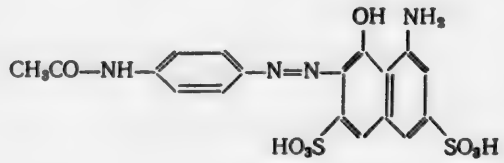
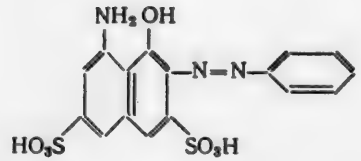
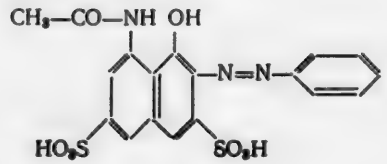
Reagent	Formula	Color of the reagent with:	
		CH_3COONa	CH_3COONa and $PdCl_2$
Anthracene red acid PG		Red-orange	Brown
Azofuchsine 6B		Red	Violet
Red acid 2B		Red	Red-violet
Red acid brilliant G		Red	Intense-red

TABLE 2 (continuation)

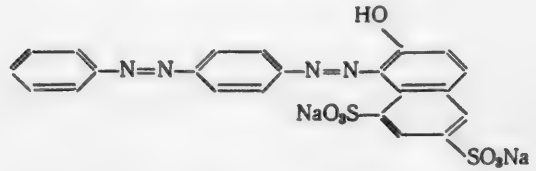
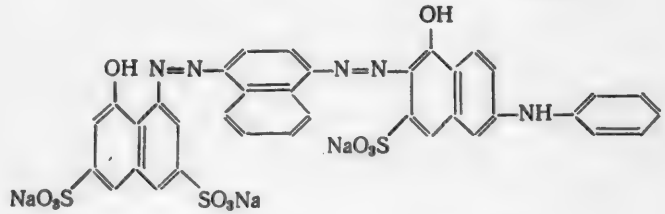
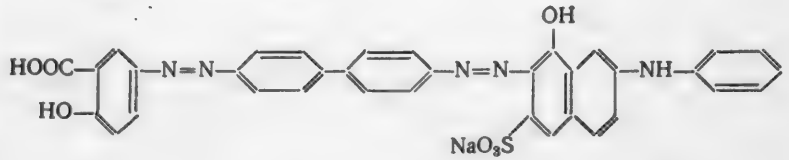
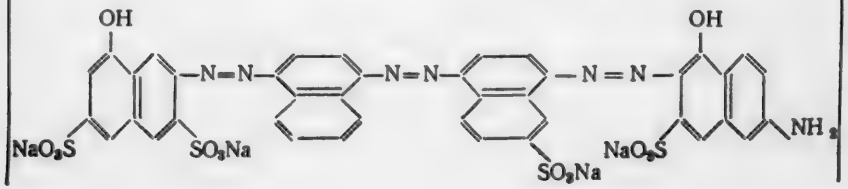
Reagent	Formula	Color of the reagent with:	
		CH_3COONa	CH_3COONa и $PdCl_2$
	B. Diazo- and polyazo dyes		
Puntsovy B. O. extra		Orange	Red
Benz light blue B		Blue	Intense blue
Diamant brown B		Brown	Red-brown
		Blue (light)	Blue

TABLE 2 (continuation)

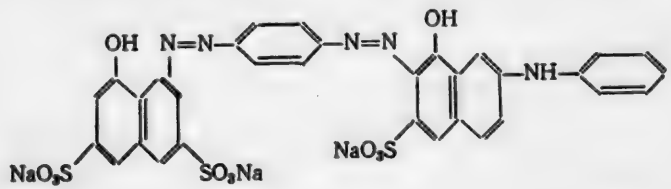
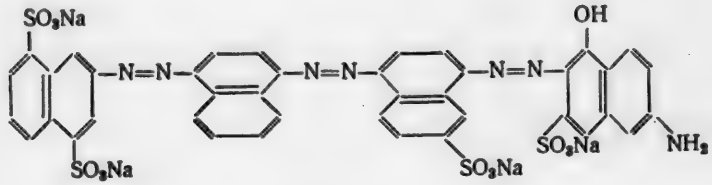
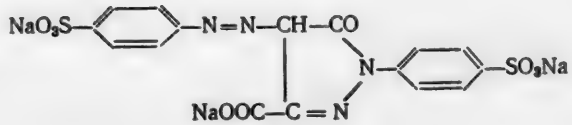
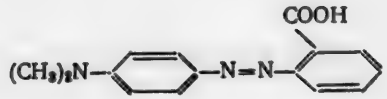
Reagent	Formula	Color of the reagent with :	
		CH_3COONa	CH_3COONa + $PdCl_2$
Benzo light violet B.L.		Violet	Blue
Lilac light blue B 2 R		Blue (light)	Blue
Tartrazine		Yellow	Brown
Methyl red		Yellow-orange	Red-violet

TABLE 3

Pd, γ	Optical density at the absorption maximum, obtained with the reagents: Benzyl orange M_{53}	Methyl orange M_{48}	Magneson I M_{57}	Methyl red M_{57}	Notes
2,5	—	—	—	0,055	2 ml of a 0.01% solution of benzyl orange in ethanol was added
4,9	—	—	—	0,11	2.5 ml of a 0.01% solution of methyl orange in ethanol was added
9,8	—	—	—	0,23	4 ml of a 0.01% solution of magneson in ethanol was added
24,6	0,05	0,075	0,075	0,57	
49,1	0,11	0,15	0,15	1,14	2 ml of 0.01% solution of methyl red in ethanol was added
98,2	0,22	0,30	0,31	—	
196,7	0,44	0,60	0,62	—	(Total volume of solution)
295,0	0,66	0,90	0,93	—	
393,3	0,88	—	—	—	

Fig. 1. Conformation of solutions of the compounds of palladium with azo dyes to Beer's law. 1) Benzyl orange. 2) methyl orange; 3) magneson I; 4) methyl red.

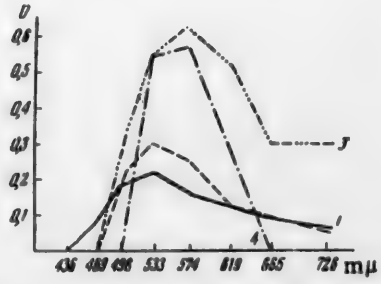


Fig. 2. Absorption curves of the compounds of palladium with azo dyes. 1) Benzyl orange, 98.33 γ Pd; 2) methyl orange, 98.33 γ Pd; 3) magneson 1; 196.66 γ; 4) methyl red, 24.58 γ Pd.

In order to settle the question of whether the wavelength at which we carried out the determinations was the most suitable (when the absorption of the solutions of reagent is a minimum), we took absorption curves on a

TABLE 4

Stoichiometric Ratio of Pd/ Benzyl Orange (spectrophotometric)

ml $PdCl_2$ 98,33 γ/ml	ml of 0.01% reagent	Optical density M_{53}
1	0,1	0,14
1	0,2	0,16
1	0,3	0,16
1	0,4	0,16
1	0,5	0,21
1	5	0,21

TABLE 5

Stoichiometric Ratio of Pd/ Benzyl Orange (refractometric method)

ml $PdCl_2$ 98,33 γ/ml	ml of 0.01 % reagent	$n_D^{25,5°}$
1	0,1	1,362412
1	0,3	1,362448
1	0,5	1,362484
1	0,8	1,362412
0	Reagent	1,361100

TABLE 6

Stoichiometric Ratio of Pd/ Methyl Orange (spectrophotometric method)

ml $PdCl_2$ 98,33 γ/ml	ml of 0.01% reagent	Optical density M_{53}
1	0,5	0,19
1	0,75	0,25
1	0,8	0,265
1	0,9	0,295
1	1	0,30

TABLE 7

Stoichiometric Ratio of Pd/ Methyl Orange (refractometric method)

ml $PdCl_2$, 98,33 γ/ml	ml of 0.01 % reagent	$n_D^{25,5°}$
1	0,5	1,36232
1	0,8	1,36261
1	1	1,36266
1	1,2	1,36259
1	1,5	1,36256
1	2	1,36245
0	Reagent	1,36181
$PdCl_2$	—	1,33257

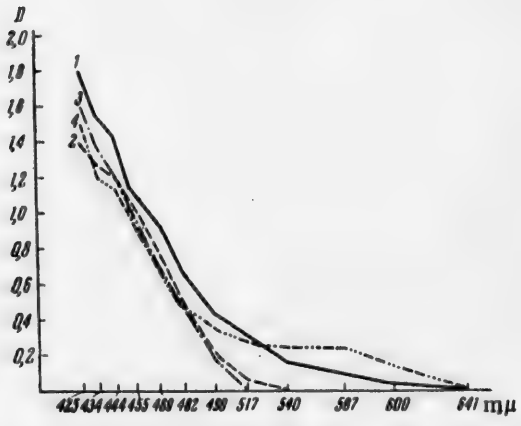


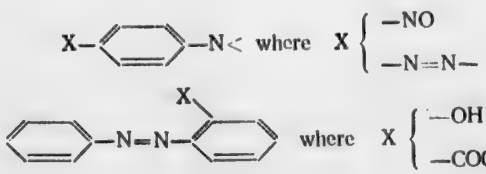
Fig. 3. Absorption curves. Benzyl orange + $PdCl_2$; 2) benzyl orange; 3) methyl red; 4) methyl red + $PdCl_2$.

monochromator. Since benzyl orange and methyl red are the most suitable for determination of palladium (the color is formed immediately and is stable with time) we took the absorption curves of these two compounds (Fig. 3) the curves taken were for benzyl orange, benzyl orange + $PdCl_2$, methyl red and methyl red + $PdCl_2$, respectively.

Methyl orange permits the determination of palladium in the presence of platinum at a ratio of 1: 14 with good results.

SUMMARY

During an investigation of 22 organic materials which react with palladium it was established that: the following are functional - analytical groups for Pd^{II}:



A photometric method of determining from 2.5 to 400 γ of Pd (II) by means of benzyl orange, methyl orange magneson I, and methyl red is suggested.

Methyl red is the most sensitive of the reagents studied; it can be used for the determination of palladium in the presence of 14 times its amount of platinum.

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RECORDING THE OXYGEN ISOTOPE RATIO IN CARBON MONOXIDE

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Conversion of a MS-2M type mass-spectrometer into a high-precision setup for recording the isotopic ratio of light elements has been dealt with in a previous communication [1]. On a setup of this type research has been carried out on the isotopes of sulfur in natural materials [1-3], and also on oxygen, for paleo-temperature purposes [4,5]. During a study of the isotopic composition of oxygen, both in terrestrial materials and in meteorites, carbon monoxide was used for recording O^{18}/O^{16} [6]. From the viewpoint of mass spectrometry, carbon monoxide has a number of characteristics.

1. Recording of O^{18}/O^{16} is carried out on the basis of masses of 30 ($C^{12}O^{18}$) and 28 ($C^{12}O^{16}$); the latter coincides with the intense background molecular mass (N_2) of the apparatus itself.

2. Mass 28, and, particularly mass 30 are superimposed by fragments of the same masses formed from the hydrocarbons used in the vacuum grease; this considerably complicates recording of the isotopic ratios of oxygen.

3. Carbon monoxide is hardly condensed at all by liquid air so that it is difficult to store it before and after carrying out an analysis.

The present article is devoted to descriptions of

a) constructional details of a receiver for the ions and of a glass attachment to the filling system for the purpose of storing the CO and introducing it into the mass spectrometer during an analysis;

b) a method for recording O^{18}/O^{16} from carbon monoxide for masses of 30 and 28;

c) the determination of the absolute ratio of O^{16}/O^{18} for CO adopted earlier as a standard [6].

Ion Receiver and the Construction of a Glass Attachment to the Filling System for Storing CO and for Introducing it into the Mass Spectrometer.

The ratio of O^{18}/O^{16} from carbon monoxide is registered as the ratio of the corresponding masses

$$\frac{30\,[C^{12}O^{18}]}{28\,[C^{12}O^{16}]}.$$

The dispersion of the MS-2M instrument is 1.35 mm for a difference of 1% in the masses, accordingly, in order to realize simultaneous reception of masses of 30 and 28, the distance between the collector slits should be adjusted to be about 9 mm.

Bearing this fact in mind, a two-collector ion receiver was designed and constructed (Fig. 1), which permitted the distance between the centers of its slits to be changed from 7 to 11 mm.

The fixed slit 3 of the receiver was arranged so that its position coincided with the central beam, while the movable slit 1 was shifted relative to it by a distance which ensured recording of a mass of 28. The slit widths were 1 and 1.5 mm respectively for the fixed and movable slits.

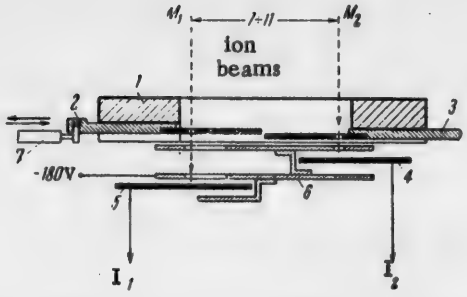

Fig. 1. General appearance of the ion-receiver. 1) Receiver base. 2) movable slit; 3) fixed slit; 4-5) collector plates; 6)suppressing box ; 7) micrometer screw.

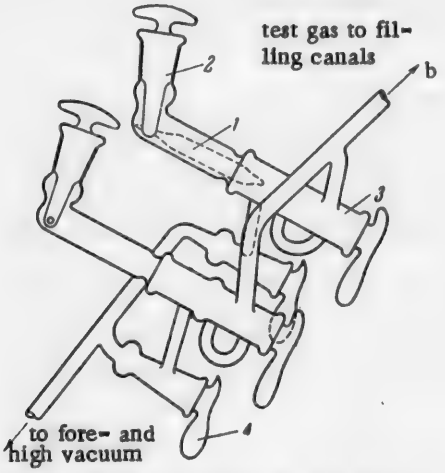

Fig. 2. Glass attachment for the filling system.

In preparing the ion receiver, particular attention was given to screening of the receiver plates 5 and 4 so that secondary electrons did not fall on them. This was achieved by preparing a screened casing 6 (Fig. 1) maintained at a potential of -180 volt.

The receiver plates and the screened casing were made from sheet tantalum 0.3 mm thick, while the rest of the elements of the receiver were made from stainless steel.

Subsequent experimental checks showed that the ion receiver completely fulfilled the purpose it was designed for. In Fig. 2 is shown an attachment — a glass attachment to the filling system — for introducing into the ion source of the mass spectrometer, both the test sample of CO and the CO used as a standard. The ampoules containing the test samples of gas are placed as shown in the diagram in the glass reservoirs. These reservoirs which are fitted with ground joints are connected to the attachment and are pumped out to give a high vacuum; before the test, by rotating the tap 2 the tips of the ampoules are broken and the gas is liberated.

The CO released from each of the ampoules is measured out by taps 3 in turn, and led into the two canals of the filling system, which each is, in turn, passed through the valve system into the mass spectrometer.

After the test gas has been measured out, the gas remaining in the reservoirs can be used for repeated determinations of the isotopic ratios, or its place can be taken by following samples.

When necessary, this attachment can also be used for the analysis of other gases, in particular, nitrogen.

Method for Recording O^{18}/O^{16} from Carbon Monoxide on Masses of 30 and 28 .

Comparison of the isotopic ratios of oxygen in test samples and in standard carbon monoxide is linked with a number of difficulties which we shall deal with briefly here, since their resolution will guarantee reliable recording of O^{18}/O^{16}. The masses 30 and 28 which are used for recording the isotopic ratios of oxygen are surrounded by a background. It has proved to be particularly troublesome in the case of mass 30 interference comes from hydrocarbon molecules from the filling system although background value did not exceed 15-17 millivolts. The mass of 30, on switching off the valves, initially slowly increased to 20-21 millivolts, and then even more slowly, in the course of minutes or more, fell to 15-17 millivolts. During recording on a self-recorder, the ratio of the 30/28 masses of the gas samples being compared, as a result of the unstable background, was almost impossible to record. In order to prevent interference from these volatile components which are responsible for the appearance of the background, it was decided to introduce a trap placed in liquid air into the filling canals. The results were contrary to expectations: the ratio of the 30/28 masses was not established, it fell as in the case where was a background of mass 30 present, although the hydrocarbons were prevented from passing into the ion source from the filling canals by freezing out with liquid air. The drop observed, even after taking this precaution, during recording of the ratio 30/28 on the self-recorder ribbon, was related to some separation of the masses on the glass traps cooled to -187°, expressed in the results as an impoverishment in masses of 30($C^{12}O^{18}$) in the test gas passing into the ion source.

On excluding the effect of the background on the isotopic ratio by cooling, a complication connected with separation of the isotopes develops which made things even worse. Recording of the ratios of the oxygen isotopes was possible only by the simultaneous exclusion of the background effect, and prevention of at least an appreciable

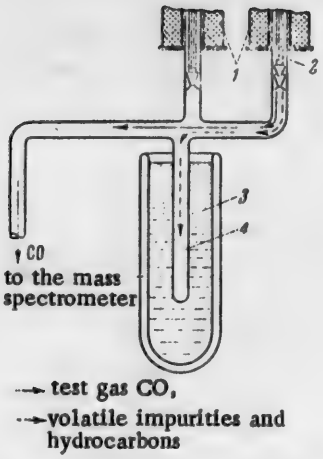

Fig. 3. Attachment for purifying CO from volatile impurities.

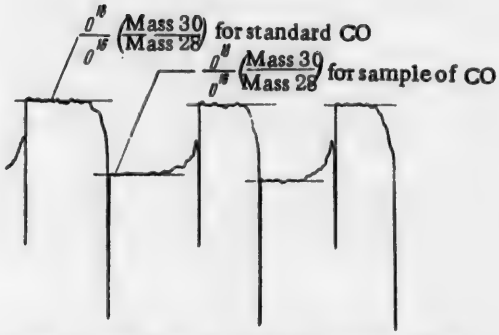

Fig. 4. Recording on the self-recorder ribbon of O^{18}/O^{16} for a sample and for a CO standard.

TABLE 1

Relation between the Nitrogen Content of CO Samples and the Difference in the Isotopic Ratios between the sample and the Standard as a Result of the Nitrogen Present.

Sample No.	Value of mass N^{14} in millivolts for:		Diff. between sample and std., %	Diff. between O^{18}/O^{16} ratios for sample & std., %
	standard	sample		
1	850	1250	47,1	4
2	900	920	2,22	0,2
Dunite 5	900	905	0,55	0,05

separation of the isotopes. If separation of the isotopes can be carried out to the same extent in both the standard and in the sample, no error will be observed. Both these conditions can be fulfilled, as shown experimentally, if immediately after the valves 2 is fitted a glass by pass trap, (see Fig. 2), 4, placed in liquid air 3 (Fig. 3) during analysis of the CO. Hydrocarbon and other volatile components are condensed in the cooled trap, while the test gas (carbon monoxide) which hardly separates at all, passes into the ion source of the apparatus. By introducing such an attachment, the background to the operating masses of 30 and 28 was depressed to 5-6 millivolts and remained stable on switching over the valves. In Fig. 4 is shown a recording of the isotopic ratios of oxygen for a sample and for a standard, which shows that the unstable effect of the background has been eliminated, and, even after switching over the valves, the preceding gas is rapidly replaced by the next sample, while O^{18}/O^{16} comes out as a straight line. The distance between the ratios for the sample and the standard is the difference sought expressed as a percentage.

Masses of 28 and 30 belonging to carbon monoxide, coincide during recording with molecular nitrogen, accordingly, during analysis, one must bear in mind the possibility of contamination of a test sample of CO by atmospheric nitrogen, when a sufficiently high vacuum is not obtained.

The presence of nitrogen as an impurity in test CO means that the recorded ratio of the masses 30/28 is "facilitated" because of the preferential superposition of N^{14}-N^{14} on the 28 mass, which is readily understable knowing the distribution of nitrogen atoms in nature [7].

Control of the presence of nitrogen in CO samples was carried out by comparing the atomic mass 14 (N^+) for a standard and for the sample. In the absence of nitrogen as an impurity in the gases being compared, the intensity of mass 14 will be the same, while in its presence (in CO samples for example), the peak for mass 14 for a sample will be higher than that for the standard in the case of levelled intensities of mass 28.

Table 1 contains as examples some results obtained for a number of samples containing various amounts of nitrogen as impurity.

As can be seen from Table 1, there exists some correlation between the amount of nitrogen present as an impurity in a sample as compared with that in standard, and the difference obtained between O^{18}/O^{16} for the standard and the sample as a result of the presence of this nitrogen.

It was found experimentally that control of CO samples on the basis of the atomic nitrogen mass guarantees the test gas to be free from contamination by nitrogen within the limits up to 0,5%, which means an error in the difference between the O^{18}/O^{16} ratios of 0,05% (Dunite 5). In the same way it is possible to control test samples of CO contaminated by nitrogen on the basis of mass C^{12}.

In order to get results as close as possible to the actual values, samples of CO were prepared independently

TABLE 2

Reproducibility of the Results of Isotopic Analysis of Oxygen for CO Samples Prepared at Different Times

Sample	Difference of the O^{18}/O^{16} ratio for sample and standard, %
"Zhovtnev Hamlet" meteorite	—0,72; —0,70
"Pallasov Iron" meteorite	—0,74; —0,74
"Saratov" meteorite	—0,75; —0,72
Dunite 5	—0,60; —0,55
Dunite 6	—0,78; —0,76
Stannern meteorite (akhondrite)	—0,80; —0,78; —0,78
Quartz, Neroik deposit, Urals	0,00; 0,00; 0,00; 0,00

twice, and sometimes three times, and were measured at different times. The agreement between the results enabled us to conclude that the isotopic ratio for oxygen for a given sample was established correctly.

Table 2 contains results for a number of independent measurements of CO samples prepared at different times.

It is clear from Table 2 that the recorded results lie within the limits of 0.02%, except in Dunite 6 where this difference amounts to 0.05% because of contamination by nitrogen, as is evident from Table 1.

In conclusion we should point out that during recording of the ratio $\frac{30\,[C^{12}O^{18}]}{28\,[C^{12}O^{16}]}$ the preamplifier resistances were fixed at 5×10^{11} ohms for a mass of 30 and at 5×10^{10} ohms for a mass of 28.

Determination of the Absolute Ratio O^{16}/O^{18} for CO Accepted as a Standard.

Nier [8] has established the absolute distribution of the isotopes of atmospheric oxygen. Results of the measurements of the isotopic ratios of oxygen from various materials, carried out by various authors, were obtained relative to standards arbitrarily chosen by these authors, the absolute ratio O^{16}/O^{18} for these standards being unknown. This fact lowers the value of these investigations considerably, since it is impossible to compare the various results. We have tried to fill this gap; for this purpose, in addition to recording the difference between the isotopic ratios of the standard and the samples, expressed in percentage, we also obtained the absolute ratio O^{16}/O^{18} for each of the samples of CO measured.

We found a method which permits a fairly accurate determination ($\pm$ 0.2 %) of the ratio O^{16}/O^{18} from carbon monoxide, using S^{32}/S^{34} obtained from SO_2 as a standard. The SO_2 was prepared by ignition of troilite (iron meteorite) for which $S^{32}/S^{34} = 22.200$, this being the same for all meteorites (stone and iron) [3]. S^{32}/S^{34} as a standard for comparing O^{16}/O^{18} was chosen for the reason that its isotopic ratio is known, and therefore by using it is is possible to exclude the discrimination of the apparatus. In addition, measurement of O^{16}/O^{18} is a very difficult problem because of the small distribution of O^{18}(0.204%). Actually, in order to obtain an intensity of several hundred millivolts for a mass of 30, the intensity of mass 28 should be expressed in hundreds of volts. Such an increase in the more widely distributed mass would lead to its deformation during recording from Coulomb interactions between the ions, leading to diffusion of the peak, discharge of ions in the receiver, and nonlinearity of the preamplifier, etc.

All this complicates accurate recording of O^{16}/O^{18}. If, therefore CO and SO_2 are introduced into the mass-spectrometer through the two canals of the filling system, and the intensities of the most widely distributed masses of oxygen and sulfur are levelled and they are excluded from all discrimination, then it should be possible, by comparing the least widely distributed masses, to determine O^{16}/O^{18}.

Let us consider the equations

$$S^{32}/S^{34} = 22.200 \qquad (1)$$

and

$$O^{16}/O^{18} = X \qquad (2)$$

TABLE 3

Results Obtained during Determination of the Absolute Ratio O^{16}/O^{18} for CO used as a Standard in [6]

Peak for mass 30 minus background	Peak for mass 30 minus the contribution $C^{13}O^{17}$	Peak for mass 50 minus background	Peak for mass 50 minus the contribution $S^{32}O^{18}$	$\frac{O^{16}}{O^{18}}$
416	415	9560	9102	486,8
536	535	12100	11544	486,4
414	413	9530	9092	488,6

By equating the intensity of S^{32} to O^{16} and excluding them from equations (1) and (2) then

$$O^{16}/O^{18} = X = 22.200 \cdot S^{34}/O^{18} \qquad (3)$$

but

$$\frac{S^{32}}{S^{34}} = \frac{48\,[S^{32}O^{16}]}{50\,[S^{34}O^{16}]}, \qquad (4)$$

Mass 50 is made up from $S^{34}O^{16} + S^{32}O^{18}$; accordingly, in order to get equation (4), it is necessary to substract 4.6 %, as the contribution of $S^{32}O^{18}$, from the recorded intensity for the peak of mass 50

and

$$\frac{O^{16}}{O^{18}} = \frac{28\,[C^{12}O^{16}]}{30\,[C^{12}O^{18}]}. \qquad (5)$$

Mass 30 is made up from $C^{12}O^{18} + C^{13}O^{17}$, accordingly, in order to get equation (5) it is necessary to subtract 0.2%, as the contribution of $C^{13}O^{17}$ from the recorded intensity of the peak for mass 30.

The experiment is carried out as follows.

Mass 30 is made up from $C^{12}O^{18} + C^{13}O^{17}$; accordingly, in order to get equation (5) we substract 0.2% from the recorded intensity of the peak for mass 30. The experiment is carried out as follows.

An M-193 voltmeter with a well-calibrated scale is connected to the output of the amplifier recording the less widely distributed masses O^{18} and S^{34}. CO is introduced into one of the filling canals and peak values are recorded simultaneously on both amplifiers – mass 30 on one, 28 on the other. SO_2 is then introduced into the second canal and masses of 50 and 48 are recorded, as in the case of the CO, on the two amplifiers. SO_2 is introduced so that the intensity of mass 48 ($S^{32}O^{16}$) is equal to that of mass 28 ($C^{12}O^{16}$).

From intensities for peaks 30 and 50 we get the ratio S^{34}/O^{18}, by deducting the background present before introduction of the gases being compared, and introducing a correction for $C^{13}O^{17}$ and $S^{32}O^{18}$, as indicated above.

Results of these measurements are given in Table 3. From them it is possible to conclude that O^{16}/O^{18} for the standard used in [6] is 487 ± 1.

SUMMARY

A design for an ion receiver capable of simultaneously recording masses of 28 and 30 is described, as well as a glass attachment for the filling system which sotres the CO to be analyzed and fills the mass spectrometer. A method is suggested for precise recording of the oxygen isotope ratio in CO, and a method is described for determining the absolute ratio O^{16}/O^{18} based on using $S^{32}/S^{34} = 22.200$ from the troilite of an iron meteorite as a standard.

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POLAROGRAPHIC DETERMINATION OF SMALL AMOUNTS OF PHENOL ON A ROTATING PLATINUM ANODE

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In recent years solid electrodes have found increasing use in polarographic analysis and for studying the kinetics of electrochemical processes [1-10].

Because of certain peculiarities of the dropping-mercury electrode, the application of solid electrodes has acquired special significance for the polarographic study and analysis of those classes of organic compounds, which are either subject to direct oxidation, or are strong oxidizing agents. Nevertheless, the practical application of solid anodes for the polarographic determination of organic compounds has come up agains a number of serious difficulties connected with the characteristics of diffusion kinetics and with specific changes in the state of the surface of the solid electrode during the process of anodic polarization. It is for this reason that this interesting problem is represented in the literature by only a few papers [1-6], while the results of these papers do not satisfy the requirements of reproducibility and accuracy of quantitative polarographic analysis.

The work described here is devoted to the polarographic determination of small amounts of phenol on a rotating platinum anode.

Experimental Technique. The following reagents were used; 1) phenol, "pure" and chemically pure grades $d_{45} = 1.0550$, $n_D^{45} = 1.5400$; 2) highly pure phenol subjected to a two-fold distillation ($d_{45} = 1.0545$; $n_D^{45} = 1.5391$); 3) production fraction – "phenol water".

The supporting electrolyte had the following composition: 0.1 M $NaNO_3$ + 0.1M H_3BO_3 + NaOH; pH 10.7 ($\pm$ 0.1).

A 1.0×10^{-3}M aqueous solution of phenol served as the original standard solution for preparing samples.

Polarographic determination of phenol was carried out on a cylindrical, rotating platinum anode the solution being kept at a constant temperature. A platinum wire 0.5-1.5 mm in diameter and 10-12 mm long was fused into a brass rod which was fitted onto the motor shaft by means of a holder. The current was fed to the electrode by means of a special attachment fitted to the motor axle. The speed of the motor was regulated and the number of revolutions of the electrode (the motor axle) kept constant by means of an autotransformer connected to a ferroresonance voltage stabilizer. For keeping the working surface of the electrode constant, a glass bead was fused on the electrode at a distance of 5-7 mm from its tip; this served as a marker for the depth to which the electrode was immersed in the solution.

The open electrolytic cell had two sections separated by a thin plug of agar-agar. One of the sections was filled with the test solution in which the platinum anode was immersed, while the other section formed the saturated calomel half-element. The resistance of such an electrolytic cell was 700-900 ohms.

Experimental Results. In an earlier paper [11] devoted to the oxidation of phenol on a platinum anode, it was established that, on the one hand, the shape and height of the phenol diffusion wave, and also the reproducibility of successive polarograms, depend to a considerable extent on the nature of the preliminary treatment of the platinum anode, while on the other hand during the time that one polarogram is being characteristic taken

"poisoning" of the electrode occurs. This poisoning was manifested by the deposition of a scarcely observable dark-brown deposit of phenol oxidation products on the electrode surface, while the diffusion current, and, accordingly, the sensitivity of the electrode with respect to the current, dropped sharply from experiment to experiment. Attempts to eliminate "poisoning" of the electrode completely by chemical treatment of the electrode surface with various organic solvents, aqua regia, hot alkali solutions, and sulfuric acid were not successful. Electrochemical treatment of the electrode was not sufficiently effective either for this purpose.

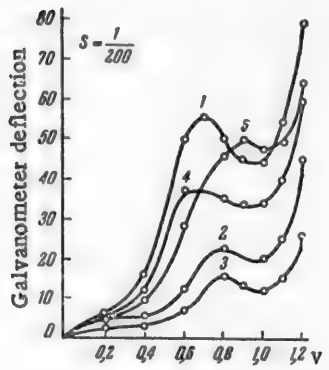

Fig. 1. Effect of the conditions used for treating the electrode on the shape of successive polarographic waves; phenol concentration 0.65×10^{-4} M; polarization rate 2.6 millivolts/second. 1) Electrode annealed for 2-3 seconds; 2) without annealing; 3) without annealing; 4) electrode annealed for 2-3 seconds; 5) coating removed and electrode annealed for 2-3 seconds.

It is clear from Fig. 1 that on all the polarograms taken in succession, in a solution containing a constant concentration of phenol, (0.65×10^{-5} M), "poisoning" of the electrode is characterized by a drop in the diffusion currents (Curves 1, 2, 3) and by the appearance of typical maxima on the polarograms.

A preliminary, short-duration (2-3 seconds) annealing of the electrode in the oxidizing flame of a gas burner only partially eliminated subsequent poisoning of the electrode (Curve 4). When the deposit was removed (by means of ashless filter paper) and the electrode annealed, in succession, a diffusion effect was observed (Curve 5).

From the results of this preliminary work it became clear that in order to develop a quantitative polarographic technique of analysis, it is of primary importance to establish the conditions for preparing the electrode which will ensure a reproducible and standard state of its surface, and also to find a method of preventing or eliminating "poisoning" of the electrode during the time when one polarogram is being taken, and during the taking of a succession of polarograms.

This problem was experimentally solved in two variants. The first variant for preparing the platinum electrode consisted of the following operations:

1) a smooth platinum electrode was treated for 5 seconds in concentrated nitric acid; 2) it was then washed tith distilled water; 3) the electrode was subjected to a three-fold stepwise anodic polarization over the range 0.0-1.5 volt. An electrode subjected once to such treatment could be kept for a long time (up to one month) in a working condition without additional preparation. After each polarogram had been taken, the brown deposit of phenol oxidation products was removed (with ashless filter paper), and the electrode annealed for a short time (about 2 seconds) in the oxidizing flame of a gas burner.

Before taking each polarogram the potential of the platinum anode was restored to the original standard value by short-circuiting to the calomel electrode.

In the second, simplified variant, anodic polarization was omitted, while the electrode was annealed for a longer time (5-6 seconds) until it was red hot. It was established that the use of either anodic treatment, or annealing of the electrode, was a necessary condition for obtaining low residual currents and a clearly defined phenol wave corresponding to a high limiting current. On the other hand, it was shown that annealing the electrode for 5 seconds not only replaces the action of anodic treatment, but, in addition, simultaneously eliminates the results of the "poisoning" of the electrode.

As a result of a study of the relationship between a number of polarographic characteristics and such factors as the state of the anode surface, the speed of rotation of the anode, the polarization rate (potential change), phenol concentration, and solution temperature, optimum conditions were found [11] for taking polarograms which were applicable to the quantitative analysis of small amounts of phenol in aqueous solutions.

The results given in the rest of this article were obtained on rotating platinum anodes rotating at a stable speed greater than 1200 revolutions/minute, and at a polarization rate of 5.0-8.0 millivolts/second.

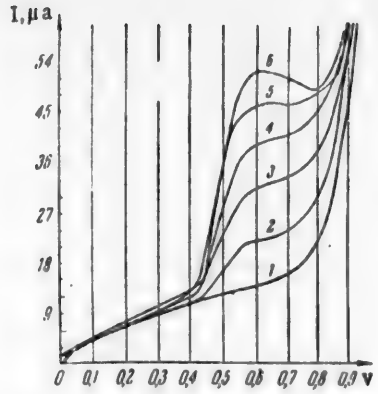

Fig. 2. Polarograms for phenol on a rotating platinum electrode. 1) Buffered supporting electrolyte; 2) phenol concentrations: 2×10^{-5}M; 3) 4×10^{-5}M; 4) 6×10^{-5}M; 5) 8.0×10^{-5}M; 6) 1.0×10^{-4}M; polarization rate 8.3 millivolts/second; t = 24°.

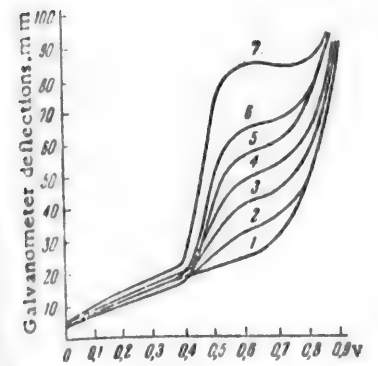

Fig. 3. Polarograms for phenol on a rotating platinum anode. 1) Buffered supporting electrolyte 0.1 M; 2) phenol concentrations: 2×10^{-5} M; 3) 4×10^{-5}M; 4) 6×10^{-5} M; 5) 8×10^{-5}M; 6) 1.0×10^{-4}M; 7) 1.5×10^{-4}M. Polarization rate 8.2 millivolts / second; t = 24°.

All potentials are referred to the saturated calomel electrode.

In Fig. 2 and 3 are shown typical series of photopolarograms for aqueous solutions of phenol within the concentration limits $1.0 \times 10^{-5} - 1.0 \times 10^{-4}$M and $1.0 \times 10^{-5} - 1.5 \times 10^{-4}$M, taken on various automatic polarographs, when two different platinum anodes were used. Readily reproducible results were obtained for each series of experiments. Fig. 4 illustrates polarograms taken on a disc diagram for $1.0 \times 10^{-5} - 1.0 \times 10^{-4}$M phenol solutions; these were taken on an indicating and recording electron polargraph of special construction, developed in the Scientific Research Institute of Synthetic Alcohols by V. I. Ginzburg and L. S. Klyainshtein.

In Fig. 5 is shown the relation between the limiting current and concentration for the series of polarograms in Fig. 3.

As is evident from Fig. 2, 3, 4 and 5, under the given conditions there are observed clearly defined diffusion waves corresponding to large limiting currents. Under these conditions, within the concentration range $1.0 \times 10^{-5} - 1.0 \times 10^{-4}$M, there is observed a linear relationship between the limiting current and concentration. Further increases in the concentration above $1.0 - 1.25 \times 10^{-4}$M lead to the appearance of maxima to a and gradual increase of the maxima on the curves, this being accompanied by a breakdown in the linear function $i_d - C$. Thus, from Figs. 3 and 5 it can be seen that at a concentration of 1.5×10^{-4}M there is an obvious maximum, while the value of the limiting current is somewhat less than that which corresponds to a strict linear relationship of the function $i_d - C$, the point on Fig. 5 is arranged slightly below the straigt line.

The experimental results indicate that it is possible, in principle, to carry out a quantitative polarographic determination of small amounts of phenol in aqueous solutions.

In order to evaluate the practical expediency of the wide use of this method for analytical purposes, we determined its accuracy by means of synthetic mixtures and production samples of phenol-containing solutions.

In Table 1 and Fig. 6 are given the results of one typical series of experiments which give an idea of the reporducibility and accuracy of the suggested polarographic method. For each sample with a known phenol concentration (wave-height $d_{45} = 1.0545$; $n_D^{45} = 1.5391$) four polarograms were taken in succession. In columns 2, 3, and 4 of Table 1 are listed the value of the limiting current (i_d), the arithmetic mean for the limiting current (i_d mean), and mean-square error of a single result (F_m^{id}). The last value characterizes the reproducibility of measurements based on the limiting current. As is evident from Fig. 6, the relation between the limiting diffusion current and concentration (according to the results of Columns 1 and 2 of Table 1) is linear. By means of the calibration curve, Fig. 6, the values of the mean square error of a single result for each concentration (F_m^c) was calculated, as well as the mean square error of a single result for all the concentration range (F_m^{id-c}), and the probable mean-square error for a series of measurements (Um^{id-c}). From comparison of the values given in Columns 4 and 5 of Table 1 it can be concluded that the mean-square error calculated on the basis of the limiting current or concentration are identical. Consequently, it can be affirmed that for polarographic methods of study based on comparison of test solutions with standard solutions (taken as a criterion of the true values), the reproducibility based on the limiting current serves as a condition sufficient for characterizing the accuracy of the method.

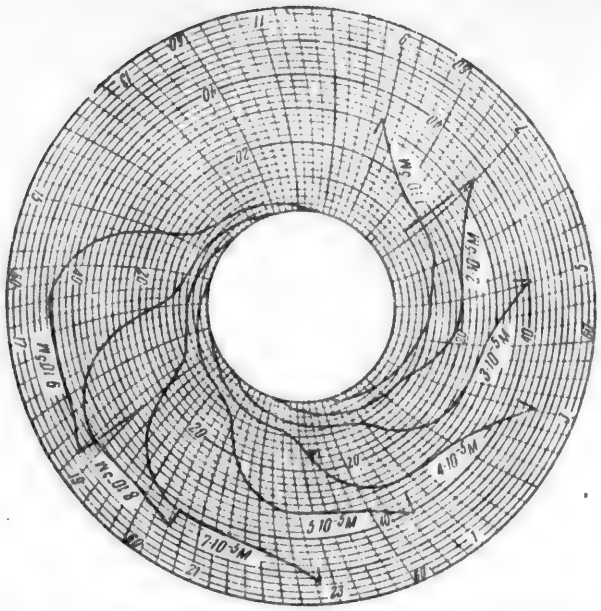

Fig. 4. Polarograms for phenol on a rotating platinum anode, taken on an electron polarograph.

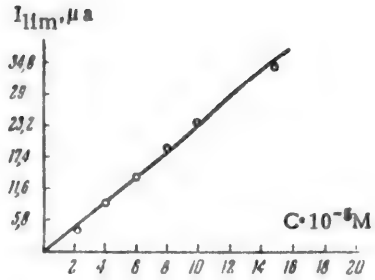

Fig. 5. Relation between the limiting diffusion current and phenol concentration when a rotating platinum anode is used. Polarization rate 6.2 millivolts/second.

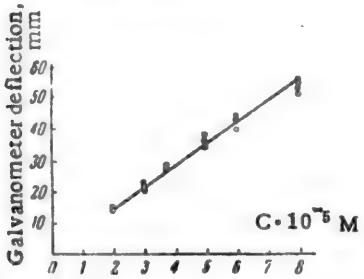

Fig. 6. Calibration curve for determination of phenol on a rotating platinum anode.

The accuracy with which the value of the diffusion current can be read visually on a Heyrovsky polarograph, type V-EOI, is 0.5 mm, which, calculated in terms of the mean-square deviation along the abscissa on the basis of the calibration curve, amounts to 3.13% and 0.78% for concentrations of 2×10^{-6}M and 8×10^{-5}M. From the results given in Table 1 it follows that the probable square error of the mean value of a series of measurements is 0.35%, i. e., it is less than the value of the square deviations. This indicates the permissible limits of random errors in a given series of experiments.

From the experimental results considered it is clear that the mean square error of a single result for various concentrations does not exceed 3.5%, while the mean-square error of a single result for all the concentration range (which characterizes the accuracy of the given method) amounts to 2.5%.

For practical purposes it was of interest to apply the present method for the direct polarographic determination of phenol in colored and turbid production media and in tap water containing other organic materials as impurities.

As test material for evaluating the practical applicability of the given polarographic method a production fraction "phenol water" was used; this fraction had, depending on technical conditions, the following composition (in % weight): phenol 4-5.5%; acetone 0.1-0.3 %; α-methyl styrene 0.8-0.1 %; acetophenone 0.5-1.0%; and H_2O 92-93 %.

As a result of carrying out a series of comparative polarographic measurements for solutions containing only phenol, and phenol plus small additions of α-methyl styrene, acetophenone, and acetone, it was established that the presence of the impurities indicated in solution does not affect the value of the limiting diffusion current, and, consequently, will not hinder the direct polarographic analysis of phenol in such production fractions.

TABLE 1

Phenol concen. mole/liter	i_d, mm	Arithmetic error, i_d, mm	Mean-square error $F_m^{i_d}$, %	Mean-square error F_m^{c}, %	Phenol concen. mole/liter	i_d, mm	Arithmetic error, i_d, mm	Mean-square error $F_m^{i_d}$, %	Mean-square error F_m^{c}, %
$2\cdot10^{-5}$	14 14,5 14 14	14,12	1,77	1,91	$5\cdot10^{-5}$	35,5 37,0 34,5 35,0	35,5	3,04	3,51
$3\cdot10^{-5}$	20,5 21,0 21,0 21,5	21,0	1,94	2,06	$6\cdot10^{-5}$	43,0 40,5 43,0 42,5	42,25	2,81	3,04
$4\cdot10^{-5}$	28,0 28,0 28,0 26,5	27,62	2,71	3,44	$8\cdot10^{-5}$	55,0 54,0 53,0 55,5	54,5	1,67	2,78

$f_m^{i_d-c}$ — Mean arithmetic error single measurement = 1,90%; $F_m^{i_d-c}$ = $= \sqrt{\frac{\Sigma f^2}{n-1}}$ — Mean-square error single measurement =2,53%; $U_m^{i_d-c}$ = $= \frac{F_m^{i_d-c}}{0,67\sqrt{n}}$ — Probable square error of mean value of a series of measurements= 0.35% = ,35%.

TABLE 2

% of phenol in phenol water	Deviation from the mean value	% of phenol in phenol water	Deviation from the mean value	% of phenol in phenol water	Deviation from the mean value
5,26	+2,5	5,38	+ 4,9	4,87	—5,1
5,57	+8,6	5,41	+ 5,4	5,32	+3,7
4,94	—3,7	5,10	— 0,6	5,01	—2,3
4.95	—3,5	5,17	+ 0,8	4,90	—4,5
5,04	—1,7	4,60	—10,0	5,45	+6,2
5,13	0,0	5,25	+ 2,3	5,07	—1,2

Note. The mean phenol content is 5.13% ; f_m = 3.3% ; Fm = 4.7% .

Table 2 contains the results of repeated polarographic determinations of phenol in the same production fraction ("phenol water"); these determinations were carried out by two workers on different platinum anodes and different polarographs. The phenol content of the test solution was determined by the comparison method. Dilution of samples to be analyzed polarographically was carried so that their phenol content was within the range 1.0×10^{-5} to 1.0×10^{-4}M. A 1.0×10^{-3}M solution of high-grade phenol was used for preparing the standard solutions.

The phenol content of the original test solution ("phenol water") was calculated by means of the formula

$$X = \frac{h_2 \cdot c \cdot b \cdot 9{,}41}{h_1},$$

where h_1 is the limiting (maximum) diffusion current of the standard sample in mm of the galvanometer scale or in μa; h_2 is corresponding value for the test solution; c is the molar concentration of the standard solution; v is the dilution of the test solution.

It follows from the results given in Table 2 that the arithmetic mean-square error of a single determination,

which characterize the accuracy of the polarographic method of analyzing phenol in "phenol water", are 3.3 and 4.7 % respectively.

It should be noted that the evaluation of the accuracy of the analytical method for determining phenol in production fractions, was deliberately carried out under the most severe conditions corresponding to the maximum possible systematic and random errors of a given series of measurements.

The experimental results obtained allow one to conclude that the accuracy of the recommended polarographic method is high enough and completely satisfies the requirements of series analysis of phenol in production fractions. It would be expedient to make wide use of such a polarographic method for the analysis of phenol, in view of its advantages over other chemical and physicochemical methods of analyzing phenol.

The method permits comparatively rapid, fairly accurate, determinations of small amounts of phenol (down to 1.0×10^{-5} M) directly in colored, turbid media, containing impurities in the form of other organic materials, in particular α-methyl styrene, acetophenone, and acetone.

SUMMARY

Optimum conditions have been established for preparing rotating platinum anodes, so that clearly defined and reproducible polarographic waves are obtained for phenol, corresponding to large limiting currents.

A new method has been developed for the polarographic determination of small amounts of phenol using a rotating platinum anode. The method can be used for the direct determination of small amounts of phenol (down to 1.0×10^{-5} M) directly in the colored, turbid media containing other organic materials present as impurities and, in particular α-methyl styrene, acetophenone, and acetone. The mean-square error of the method is 2.5-4.7 %.

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ANALYSIS OF NITROPARAFFINS BY PARTITION CHROMATOGRAPHY

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Determination of individual nitroparaffins in their mixtures is one of the very difficult problems of analytical chemistry. Methods based on reduction of the nitroparaffins only permits determination of their sum [1-9]. The same is almost true of polarographic methods [3-7]. Methods based on differences in the behavior of primary, secondary, and tertiary nitroparaffins toward alkalis only permit the possibility of group analysis [1,8]. A rapid method of determining nitroparaffins based on their chlorination [9], according to the authors themselves, can only be applied for the determination of functional groups and then only in the absence of compounds which can be oxidized or chlorinated. Wider possibilities are opened up by the photometric method [10-16], but even this does not ensure complete analysis of a mixture, even of the simplest nitroparaffins (C_1-C_3). In a number of cases only total nitroparaffins can be determined by this method. Of the individual nitroparaffins, 2-nitropropane [10] and nitromethane [11,14,16] can be determined with reasonable confidence. When nitroethane and 1-nitropropane are present simultaneously only their sum can be determined [11,13].

A mass-spectrometric method described recently [17] requires complicated equipment. The relative closeness of the boiling points of the nitroparaffins complicates their analysis by fractionation also.

We tried to use partition chromatography for separating a mixture of the simplest nitroparaffins (C_1-C_3). The nitroparaffins were reduced to the corresponding amines, the mixture of which was then separated chromatographically. The reduction rate of the simplest nitroparaffins is approximately the same (Table 1).

Thus, the percentage proportion of the amines obtained, does not differ in practice from the proportions of the nitroparaffins in the mixture prior to reduction. Knowing the total alkylamine content and the amount of each of the alkylamines, it is possible to determine the percentage composition of the nitroparaffins.

The total content of alkylamines is readily determined by titrating a mixture of their salts with alkali in an aqueous acetone medium, a small amount of formalin being added toward the end of titration [18]. The individual alkylamines in the mixture obtained can be separated by partition chromatography. The application of this method for separating mixtures of primary, secondary, and tertiary alkylamines with carbon chains of the same length, has been described in the literature [19-21]. The same principle, with some modifications to the analytical method, can be used also for separating mixtures of primary alkylamines with carbon chains of different length.

EXPERIMENTAL PROCEDURE

Any method which permits nitroparaffins to be reduced to the amines at the same rate can be used for reducing the nitroparaffins. We used the method of Johnson and Degering [22], and established that by using sufficiently active reduced iron, the process is completed considerably more rapidly than the authors indicated.

The amines obtained, after the reaction solution has been made alkaline, were distilled into 0.5 N sulfuric acid. The solution was evaporated to 10 ml. 1 ml of the solution obtained was placed in a 250 ml flask. Free sulfuric acid was neutralized with 0.1 N NaOH. The amount of the latter required was determined beforehand by titration of a separate aliquot with alkali using methyl red as indicator. To the neutralized solution was added 35 ml of acetone neutralized with respect to phenolphthalein and the mixture titrated with 0.1 N NaOH until a pale-rose color was obtained. 5 ml of formalin neutralized with respect to phenolphthalein was then added after which the solution was again titrated to a pale rose color; the amount of alkali used corresponds to the total content of alkylamines in the test solution.

TABLE 1

Yield of Amines During Reduction of Various Nitroparaffins by Iron and Hydrochloric Acid

Nitroparaffin	Taken, g	Iron used up for the reduction, g	Reduction time (hours)	Yield of amine, %
Nitromethane	0,5	30	6	100,7
Nitroethane	0,5	30	6	97,0
1-Nitropropane	0,5	30	6	97,6
2-Nitropropane	0,5	30	6	100,7
Nitromethane	1,0	10	4	91,4
Nitroethane	1,0	10	4	93,7
1-Nitropropane	1,0	10	4	94,2
2-Nitropropane	1,0	10	4	94,1

TABLE 2

Separation of Mixtures of the Salts of Primary Alkylamines Obtained by the Reduction of the Corresponding Nitroparaffins

Mixture No.	Comp. of orig. mix.		Nitroparaffins found		Relative error
	Components	%	0.05 N HCl used, ml	amount, % %	
1	1-Nitropropane	55,9	12,6	53,0	—5,2
	Nitroethane	44,1	11,2	47,0	+6,5
2	1-Nitropropane	43,4	10,9	42,2	—2,7
	Nitroethane	56,6	14.9	57,8	+1,1
3	1-Nitropropane	49,9	8,6	46,5	—6,8
	Nitroethane	42,6	8,5	45,9	+7,7
	Nitromethane	7,5	1,4	7,6	+1,3
4	2-Nitropropane				
	1-Nitropropane	47,9	13,0	45,0	—6,0
	Nitroethane	43,4	13,2	45,7	+5,3
	Nitromethane	8,7	2,7	9,3	+7,5

Chromatographic Procedure. 35 g of air-dried starch carefully mixed with 0.35 g of calcium oxide calcined at 700-800°. To this mixture water was added, so that on taking the moisture content of the starch into consideration, the final water content of the mixture was 60% with respect to the absolutely dry starch. To this mixture was added 28 ml of chemically pure benzene and the mixture again carefully mixed. A chromatographic column was filled with this mixture in stages. The density of the column was regulated so that using the given amount of starch and a tube with a diameter of 17-18 mm the height of the column was 18 cm. Directly on top of this layer was placed a second layer, consisting of 2 g of starch, 0.9 g of calcium oxide which had not been calcined, and 1 ml of water. The height of the top layer was 1.5-2.0 cm.

1 ml of the test aqueous solution of the amine salts was introduced into the chromatographic column. A pressure of 180 mm was set up in the system. The mobile phase used was either butanol, or, in the case of multicomponent systems, a mixture of butanol and benzene in the proportion of 30: 70. The eluate was collected in a flask containing 15-20 ml of water containing 2-3 drops of bromothymol blue and was continuously titrated with 0.05 N hydrochloric acid.

The first to issue from the column was combined n- and i-propylamines which have the lowest partition coefficient; these were followed by ethylamine, and last methylamine. The end of the elution of one amine and the beginning of the elution of the next amine was evident from the temporary cessation in expenditure of acid for titration when a continuous supply of the mixture of butanol and benzene was passed through the column. When the titration results are presented graphically, they appear in the form of series of steps on a curve relating amount of acid used and amount of benzene supplied. The amount of the individual amines (and, consequently, of the original nitroparaffins) was calculated by means of the formula

$$\frac{a \cdot 100}{2 \cdot b},$$

where a is the amount of 0.05 N acid used in titrating the eluate issuing from the column from the beginning until the appearance of the first step (for determination of the amount of nitropropanes); from the first step to the second (for calculating the amount of nitroethane), and from the second step to the end (for the determination of the amount of nitromethane); b is the amount of 0.1 N alkali used for titrating total amines during determination of total basicity.

Results for the analysis of mixtures of the nitroparaffins are given in Table 2.

The chromatographic method described does not permit the possibility of a separate determination of the 1- and 2-nitropropanes, since the partition coefficients of the corresponding amines in the systems water-organic solvents are very close. Nevertheless, 2-nitropropane is readily determined photometrically [9]. Combination of the chromatographic method with the photometric method makes it possible to determine all the components of a four-component system fairly rapidly and without the use of complicated apparatus.

Table 3 contains the results for an analysis of two four-component mixtures, obtained by the chromatographic and photometric methods.

TABLE 3

Analysis of Mixtures of Nitroparaffins

Sample no.	Analytical method	Found, %					
		1-and 2-nitropropanes	nitroethane	nitromethane	2-nitropropane	1-nitropropane	total
1	Chromatography	73,0	16,4	10,6	—	—	—
	Photometry	—	—	—	27,7		
	Combination of chromatography and photometry		16,4	10,6	27,7	45,3	100,0
2	Chromatography	59,6	23,6	16,7	—	—	—
	Photometry	—	—	—	27,6		
	Combination of chromatography and photometry		23,8	16,7	27,6	32,0	100,1

SUMMARY

It has been shown that it is possible to use partition chromatography for the analysis of mixtures of primary alkylamines with carbon chains of varying lengths.

The accuracy of the analysis is determined by the accuracy of the chromatographic separation of the alkylamines and amounts to ± 5-7% relative, on the average.

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DETERMINATION OF CARBONYL COMPOUNDS BY MEANS OF THE REACTION WITH AMINES

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The reaction between aldehydes and amines, leading to the formation, as a rule, of anils or Schiff bases $RCHO + H_2NR_1 \rightarrow RCH{:}NR_1 + H_2O$ was suggested by Schiff [1] for the quantitative determination of primary amines. The method consists of titrating the amine with a solution of enanthic aldehyde; the end point is taken as the cessation of the appearance of a turbidity from the water liberated at the point where the titrant drops into the solution. In the course of many years this reaction has not found application in the quantitative analysis of either amines or aldehydes. Only in 1944 was this method suggested for the determination of various amines, the water liberated during the reaction being determined by titration with Fischer reagent [2]. Two articles were published in 1953 in which the same reaction was used, but for the determination of aldehydes [3,4]. The amount of aldehyde is measured from the amount of amine used up, the latter being determined by titration, in the first article potentiometrically, in nonaqueous solvent by means of a solution of salicylaldehyde [3], in the second article by a solution dioxanesulfurtrioxide (the complex of sulfur trioxide and dioxane). Laurylamine [3] and aniline [4] were used as the amines. The authors of both articles came to the same conclusion, namely, that their methods are only applicable for the determination of aromatic aldehydes.

Apparently, the anils of aliphatic aldehydes are less stable than those of aromatic aldehydes and are destroyed during titration with acids. During the potentiometric titration of aliphatic aldehydes it has not been possible to get a jump on the curve.

We made it our aim to find conditions which will also ensure determination of aliphatic aldehydes by the reaction with amines. Doubtless, the formation of anils accurs quantitatively in the case of aliphatic aldehydes also, this being shown by complete liberation of water during a Schiff titration [1], and by the results of work [5] on the determination of citral, citronellal, and cinnamic aldehyde by the reaction with aniline, the amount of aldehyde being estimated in this case on the basis of the amount of water liberated during the reaction, the water being distilled from the reaction mixture and measured in a Dean and Stark apparatus.

It seemed to us that for the determination of aliphatic aldehydes it would be more expedient to measure the amount of water liberated during the reaction, and not the amount of amine used up. Determination of water could be carried out most accurately, of course, by titration with Fischer reagent [7].

Some authors are mistakenly of the opinion that is impossible to determine water by the Fischer method in the presence of carbonyl compounds [6], and are convinced that it is necessary to convert tha latter beforehand into the cyanhydrins. Nevertheless, the author of the Fischer method has indicated that it is possible to titrate water directly in carbonyl compounds.

Table 1 contains some of our results on the direct determination of the water content of various aldehydes. The accuracy of the determination was established by titrating known amounts of water added beforehand to the aldehyde.

The reaction between Fischer reagent and aldehydes is so slow that it does not interfere with water determination. The choice of an amine for reacting with the aldehydes is determined by two considerations: the amine

TABLE 1

Aldehyde	Weight taken, g	Fischer reagent used, ml*	Water content of the aldehydes	Added water found, g
Lauric	0,2710	3,02	2,0	
»	0,2710			
+ water	0,015	11,88	2,0	0,0159
Methylnonylacetaldehyde	0,5140	1,3	0,05	
»	0,5140			
+ water	0,0144	9,30	0,05	0,0144
Citral	1,010	2,94	0,53	
»	1,010			
+ water	0,0174	12,66	0,53	0,01745
Methoxybenzoic	1,1571	3,3	0,51	
»	1,1571			
+ water	0,0202	14,51	0,51	0,02018
Piperonal	1,065	0,59	0,5	
»	1,065			
+ water	0,0160	9,49	8,5	0,01602

* In terms of a millimolar solution; 1 ml = 1,8 mg water.

TABLE 2

Aldehyde	Weight taken, g	Fischer reagent used ml	Found, % by reaction with amine	Found, % by oxime formation
Benzaldehyde	0,4813	44,5	98,2	98,6
»	0,3200	30,15	99,9	100,2
Vanillin	0,3083	20,5	101,2	100,5
»	0,2300	15,0	99,3	
Piperonal	0,2076	13,8	99,7	100,2
»	0,3463	23,3	100,7	
Methoxybenzaldehyde	0,3495	25,3	98,6	99,5
Salicylaldehyde	0,4925	39,85	96,9	98,5
Nitrobenzaldehyde	0,1063	6,98	99,5	
»	0,2253	14,97	100,5	100,0
Dimethylaminobenzaldehyde	0,2639	17,7	100,0	100,0
»	0,2770	18,6	100,1	
Enanthic aldehyde	0,3062	24,2	90,1	91,3
Methylnonyl acetaldehyde	0,0924	4,95	98,7	99,5
n-Isopropylmethylhydrocinnamic aldehyde	0,1294	6,48	94,9	96,6

should react fairly rapidly with the aldehydes, and should have a high dissociation constant so as not to interfere with the direct titration of the reaction mixture — in which the amine is in excess — with Fischer reagent. The most suitable amines were found to be aniline and o-toluidine, depending on the conditions.

Our studies showed that aromatic aldehydes react quantitatively with o-toluidine, immediately after addition of a benzene solution of the amine, while the water which is liberated during the reaction can be titrated with Fischer reagent directly in the reaction mixture. There is no need to wait for 30 minutes or one hour, as suggested previously.

Table 2 contains results obtained during the direct titration of the water liberated during the interaction of aldehydes with o-toluidine. Some aldehydes-enanthic aldehyde, citral, α-methyl, n-isopropyl, hydrocinnamic, and methylnonylacetaldehyde — also react quantitatively, but considerably more slowly during the gradual titration of water. Such a determination is not convenient, since, as test showed, the free amine also reacts with Fischer reagent. Accordingly, we should like to suggest another method for the determination of aliphatic aldehydes.

The amount of water liberated during the reaction is determined after its removal from the reaction mixture by distillation with benzene. Complete removal of such small amounts of water (30–40 mg) by distillation presented great difficulty.

TABLE 3

Weight of water, g	Benzene distilled over, %	Water found, % in the distillate	in the residue
0,0422	50	50,1	49,7
0,0480	60	68,0	31,8
0,0372	86,5	75,0	24,9
0,0310	100,0	97,0	2,75
0,0406	100,0	99,7*	
0,0425	100,0	99,8*	

* In the presence of aniline.

A study of the conditions necessary for the quantitative distillation of water was carried out on aliquots of water alone. It would appear on the basis of the azeotropic ratios for mixtures of benzene and water (91.17 : 8.83 % wt.) that such small amounts of water should come over completely with the first drops of benzene; however, as experiment showed, water is quantitatively distilled over, only when all the benzene used as the solvent has been distilled over. Presumably this phenomenon can be explained by the formation of a solution of water in benzene. An apparatus with ground glass joints was used for distilling the water.

Table 3 contains the results obtained during a study of the conditions necessary for complete distillation of water. These conditions were observed during the determination of aliphatic aldehydes. Both o-toluidine and aniline can be used as the amine in this case.

By distilling the water it was established that the reaction with amines proceeds quantitatively for all the aldehydes studied (Table 4) — both aliphatic and aromatic — and that this technique can be used as a method for the determination of these aldehydes.

Aromatic ketones of the acetophenone type do not react with amines, and, accordingly, do not interfere with the determination of the aldehydes (Table 5). The method is being studied further.

Determination of the Water Content of Aldehydes. An aliquot of the aldehyde (liquid aldehydes -directly; solids-in solution in methanol) was titrated with Fischer reagent until the first distinct appearance of the color of iodine.

In order to check on the accuracy of the determination, a known amount of water (0.015-0.020 g) was added to an aliquot of the aldehyde whose % H_2O had already been established, and this water again titrated with Fischer reagent.

TABLE 4

Aldehyde	Weight, g	Fischer reagent used, ml	Aldehyde found, % by reaction with amines	by oxime formation
Acetaldehyde	0,089	19,0	94,0	94,5
Formaldehyde	0,0933	11,0	35,4	35,0
Propionaldehyde	0,0833	9,65	67,0	67,0
Enanthic aldehyde	0,3148	26,7	96,8	96,2
»	0,3225	27,35	96,7	
Methylnonylacetaldehyde	0,4780	26,0	100	
»	0,1185	6,36	98,5	99,5
Citral	0,1910	12,55	99,8	
»	0,2682	17,69	100,3	99 0
Citronellal	0,3570	22,4	97,0	
»	0,2825	17,75	96,8	96,5
Hydroxycitronellal	0,2570	15,2	102,0	
»	0,1784	10,55	102,1	99,0
Cinnamic aldehyde	0,3898	28,95	98,0	
»	0,4122	30,1	96,5	96,0
α-Methyl-n-isopropylcinnamic aldehyde	0,1736	8,79	96,3	96,6
»	0,2542	12,9	96,5	
α-Amyl-n-isopropylcinnammic aldehyde	0,3503	15,9	91 8	
»	0,1631	7,44	92,2	92,0
Benzaldehyde	0,2319	21,3	97,3	96,8
Vanillin	0,1549	10,18	99,9	100,3
Methoxybenzaldehyde	0,1487	10,9	99,6	100,5
Piperonal	0,1540	10,21	99,5	99,9
Salicylaldehyde	0,2450	19,94	99,2	99,5
Protocatechuic aldehyde	0,1279	9,27	100,0	
Nitrobenzaldehyde	0,2852	18,9	100,0	99,8

Determination of Aldehyde by Direct Titration. To 0.2-0.4 g of aldehyde was added 5-10 ml of a 15% solution of o-toluidine or aniline in benzene, after mixing, the mixture was immediately titrated with Fischer reagent to a distinct brown color. A blank was carried out at the same time. The water content of the aldehyde was determined on a separate aliquot:

$$\% \text{ aldehyde} = \left(\frac{(a-b)\cdot T\cdot 100}{W} - c\right)\cdot\frac{M}{18},$$

where a is the amount of Fischer reagent used up for the test solution, in ml; b is the amount of Fischer reagent used up for the blank, in ml; T is the titer of the Fischer reagent expressed in g of water; W is the weight of aldehyde, taken; c is the moisture content of the aldehyde, in %; M is the molecular weight of the aldehyde.

In all cases the purity of the aldehyde was checked by formation of the corresponding oxime [8].

A Study of the Conditions for Distilling Off the Water. The apparatus used for distilling the water consisted of a pear-shaped flask ~ 100 ml, connected by means of bent tube to a condenser, which was connected in turn through an adapter provided with a calcium chloride guard tube, to the receiver – a 50-100 ml conical flask; all connections were made of ground glass.

An aliquot of water (30-40 mg) was placed in the flask and 15 ml of benzene added; in the last two experiments (Table 3) 1.25 g of aniline was added in each case. In order to keep the temperature constant the flask was heated on a vaseline bath. When a temperature of 150° had been reached heating was stopped and the flask kept at this temperature for some time; the flask was then removed from the bath but was not disconnected from the apparatus; after cooling to room temperature, the flask was disconnected and the condenser washed, by passing 15 ml of anhydrous methanol through the connecting tube which was turned round; the distillate collected in the receiver, and the residue in the distillation flask were titrated separately with Fischer reagent. Washing with methanol was essential since a considerable part of the water was held in the condenser.

TABLE 5

Carbonyl compounds	Aldehyde content of the mixture, %	
	taken	found
Acetophenone		
Benzaldehyde + acetophenone	65,4	67,0
Methylacetophenone		
Benzaldehyde + methylacetophenone	65,3	65,9
Ditto	29,1	28,7
» »	9,9	10,6
Methoxyacetophenone		
Benzaldehyde + methoxyacetophenone	64,5	65,7
Ditto	25,4	25,0

A General Method for the Determination of Aldehydes (Aromatic and Aliphatic). To 0.15-0.4 g of the aldehyde was added 15 ml of a solution of aniline in benzene; the flask, connected beforehand to the apparatus, was placed in a vaseline bath and heated to 40-60°; the water was then distilled off as described above and the condenser washed down with methanol.

A blank experiment was run in parallel in which no aldehyde was used, while the moisture content of the aldehyde was determined separately.

Determination of Certain Ketones and Their Mixtures with Aldehydes. Determination was carried out on the basis of the reaction with a benzene solution of o-toluidine, the water being titrated directly in the reaction mixture.

SUMMARY

It has been shown that both aromatic and aliphatic aldehydes react quantitatively with amines to liberate one molecule of water. Measurement of the amount of water liberated during this reaction can serve as a method for the quantitative determination of the aldehyde. It has been shown that it is possible to carry out a direct determination of the water content of aldehydes by means of Fischer reagent.

Two methods are suggested for the determination of aromatic and aliphatic aldehydes on the basis of their reaction with amines, followed by titration of the water with Fischer reagent.

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BRIEF COMMUNICATIONS

THE SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM IN URANIUM

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The necessity very often arises in analytical practice of determining small amounts of magnesium in uranium and its compounds. The present article is devoted to a discussion of the use of a very sensitive reagent for magnesium — eriochrome black T — for this purpose.

Eriochrome black T (or chromogen black special ET-00) gives colored complexes with many cations. Several authors have used eriochrome black T for the determination of magnesium in various materials [1-5]. Nevertheless no method has been published for the determination of magnesium in solutions of uranyl salts.

Working Solutions and Apparatus. A 0.1% solution of eriochrome black T was prepared by dissolving an aliquot of the purified, recrystallized [6] dye in twice-distilled methanol. Such a solution is stable for more than two months.

An ammoniacal buffer solution with a pH of 10.2 was prepared by dissolving 54 g of twice recrystallized ammonium chloride in 500 ml of 25% aqueous ammonia, and making the volume up to one liter. Working solutions of uranium were prepared from spectrographically pure uranyl nitrate; the solutions were standardized gravimetrically. All experiments were carried out in quartz vessels using specially purified water. Spectrophotometric measurements were made on a Beckman type "DU" spectrophotometer. A type LP-5 tube potentiometer was used for measuring the pH by means of a glass electrode.

The Stability of Aqueous Solutions of Eriochrome Black T and of its Complex with Magnesium. A study of the stability of aqueous solutions of eriochrome black T and of its complex with magnesium is essential in order to assess the permissible length of time between preparation of the solutions and measurement of their optical density. Such experiments were carried out by adding 3 ml of the ammoniacal buffer solution and 1 ml of the 0.1 % solution of eriochrome black T to 30-40 ml of a solution with a known magnesium sulfate content. The optical density of the solutions was measured in the course of 4 hours at various wavelengths.

These experiments showed that the optical density of solutions of eriochrome black T in a pure form, or with additions of various amounts of magnesium, decrease linearly with time to the extent of 0.3-0.8% in 30 minutes. No increase in density was observed in any of the tests; it may be assumed therefore that the equilibrium of complex-formation is established rapidly.

Determination of the Composition of the Complex*. In order to choose the optimum wavelength region, light absorption curves were taken for a solution of pure eriochrome black T, and of a solution of the dye containing magnesium in sufficient excess to suppress dissociation of the complex. As is evident from Fig. 1, the greatest difference in the optical densities of the solutions of eriochrome black T and of solutions of its complex with magnesium is observed at 500-550 mμ and 640-690 mμ. However, only the spectral region at 500-550 mμ is suitable for accurate measurements, since at wavelengths of 640-690 mμ the results show poor reproducibility.

* D is the optical density of the solution; M is the molar concentration of a solution of the compound whose formula is given below to the right of the designation; E is the molar extinction coefficient of the solution of the same compound; n is the number of molecules of eriochrome black T which interacts with one ion of magnesium.

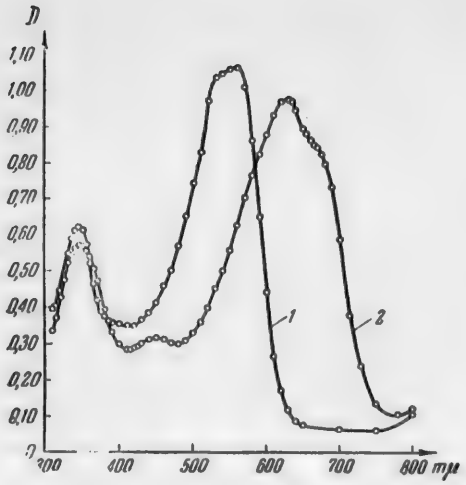


Fig. 1 . Light-absorption curves for a solution of pure eriochrome black T (Curve 2) and a solution of the latter containing excess magnesium (curve 1).

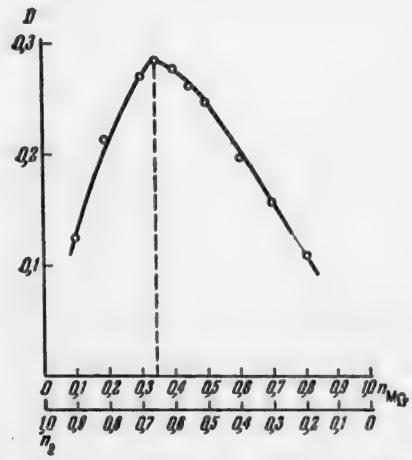


Fig. 2. Deviation of the optical density from additivity composition of the solution. D) Deviation of the optical density of a solution of eriochrome black T and magnesium from additivity; n_E) the molar fraction of eriochrome black T in solution; n_{Mg}) the molar fraction of magnesium in solution.

The composition of the complex formed between magnesium and eriochrome black T at a pH of 10 was studied by the Ostromyslenskii-Job method [7,8] and by calculation.

By means of a rigorous mathematical analysis N. P. Komar' [9] has shown that the Ostromyslenskii-Job method is not applicable to all cases. In our case this method is applicable in the form in which it is used for the study of the composition of compounds formed from colored reagents.

As is evident from Fig. 2, maximum deviation of the optical density from additivity is observed at molar ratios of eriochrome black T to magnesium of 2: 1, i. e. the complex formed has a composition expressed by the formula $(MgE_2)^{4+}$ (where E represents the anion of the dye).

Similar curves were also obtained at 500, 510, 530, and 540 mμ. In the course of this work it was established that the position of the maximum is independent of the wavelength at which the optical density is measured. Obviously, one can conclude from this that only one complex occurs in solution at pH 10; this is confirmed by published data [1,8].

In Fig. 3 are given the curves relating optical density of the solution to magnesium concentration for a constant concentration of the dye of 4.67×10^{-5} mole/liter. The composition of the complex can be calculated from this curve also.

Actually, the optical density D of a solution with an initial concentration M_E of eriochrome black T and a concentration M_{MgE_n} of the complex, at a wavelength for which the molar extinction coefficients of the dye and the complex are E_E and E_{MgEn} respectively, will be determined by the equation

$$D = (M_E - nM_{MgE_n})E_E l + M_{MgE_n} \cdot E_{MgE_n} l, \qquad (1)$$

where n is the stoichiometric coefficient of the reaction for the formation of the complex.

The values of E_E and E_{MgEn} can be determined by measuring the optical density of a solution of the dye to which no magnesium has been added (D_0), and of a solution of dye containing excess magnesium (D_0'), sufficient to suppress dissociation of the complex

$$E_E = D_0/M_E l, \qquad (2)$$

$$E_{MgE_n} = D_0' n/M_E \cdot l. \qquad (3)$$

Simultaneous solution of equations (1), (2), and (3) gives the expression:

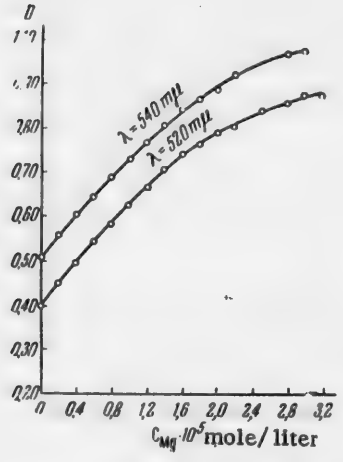
$$n = \frac{(D - D_0)M_E}{(D_0' - D)M_{MgE_n}}. \qquad (4)$$

If the initial concentration of magnesium M_{Mg} is small in comparison with the concentration of the dye, then almost all the magnesium will be combined as the complex, i. e. $M_{Mg} \cong M_{MgE_n}$, and expression (4) can be written in the form

$$n = \frac{(D - D_0)M_E}{(D_0' - D_0)M_{Mg}}. \qquad (5)$$

Cation impurities (in excess, 100 × Mg concentration)	Magnesium taken, γ	Magnesium found, γ	Relative error, %
—	4,73	4,87	3,0
—	9,45	9,29	1,7
—	9,45	9,48	0,3
—	4,73	4,67	1,3
Fe^{3+}	7,43	4,65	1,7
Co^{2+}	9,45	9,44	0,1
Ni^{2+}	9,45	9,71	2,7
Cr^{3+}	4,73	4,67	1,3
Al^{3+}	9,45	9,68	2,4
MoO_4^{2-}	4,73	4,82	1,9

Fig. 3. Relation between optical density of the solution and magnesium concentration for a constant concentration of eriochrome black T. D) The optical density of the solution; C_{Mg}) magnesium concentration, mole/liter.



The expression derived describes the initial linear parts of the curves Fig. 3. Calculations on the basis of points located on these parts of the curves gave the following values of n: 1.86 1.88; 1.92; 1.92 (λ = 520 mμ) 2.10; 2.10; 2.02, 2.02 (λ = 540 mμ) respectively for C_{Mg} 0.15 × 10^{-5}; 0.2 × 10^{-5}; 0.3 × 10^{-5} and 0.4 × 10^{-5} mole/liter, i. e., n ≈ 2.

Thus, it has been shown by two methods that the composition of the complex of eriochrome black T and magnesium is represented by a ratio of 2: 1. The result obtained agrees with those of Harvey, Komarmy, and Wyatt [1] and contradicts those of Schwarzenbach and Biedermann [6].

The Accuracy of the Determination of Magnesium in its Pure Solutions. When certain conditions are observed the maximum experimental error for determination of magnesium does not exceed ± 3%. The requisite conditions are the following:

1. The magnesium concentration of the test material should lie within the limits 0.1-0.4 γ/ml. The necessity for conforming to such a comparatively narrow range of magnesium concentrations is explained on the one hand by the intense color of eriochrome black T, and on the other hand, by the comparatively low stability of the complex formed at the very high sensitivity of the reaction.

2. The pH of the test solution must be accurately controlled. The pH must be kept within the limits 9.8-10.6. Since the optical density of the solution is strongly dependent on the acidity, deviation of the pH of the test solution from the value at which the calibration curve is taken should not exceed the limits of ± 0.1.

3. The optical density should be measured very soon after preparing the solution. If the solutions are allowed to stand for more than 30 minutes, the results obtained may be appreciably low.

4. Only twice-distilled water and purified reagents should be used. If this condition is not observed the results obtained will be appreciably high.

Procedure for the Determination of Magnesium in the Presence of Uranium. Uranium, even in small amounts interferes with the determination of magnesium, since it interacts with eriochrome black T to form a colored product. Interference from uranium can be suppressed by masking it with ammonium carbonate or hydrogen peroxide. The presence of carbonate ions in solution, however, leads to low results for magnesium. Hydrogen peroxide on the other hand rapidly destroys eriochrome black T.

Accurate determination of magnesium in uranium is possible after removal of uranium from solution by precipitation with 8-hydroxyquinoline at a pH of about 5 [10]. All the magnesium remains in the filtrate under these conditions. Excess 8-hydroxyquinoline and traces of uranium can be removed by extraction with chloroform. Such ions as Fe^{3+}, Cr^{3+}, Co^{2+}, Al^{3+}, MoO_4^{2-}, and Ni^{2+}, which occur in uranium as impurities, are coprecipitated with the uranium and do not interfere with magnesium determination.

As a result of experimental work, the following method has been developed for the determination of magnesium in the presence of uranium.

Test solution containing not less than 5 γ of magnesium is placed in a quartz beaker. After neutralization of excess acid, the volume of the solution is made up to 20-25 ml, and to it is added 5 ml of acetate buffer (10 ml

of concentrated HCl added to 380 ml of a 50% solution of CH_3COONa and the volume made up to 1 liter). The solution is heated to 70-90° and a 10 % solution of 8-hydroxyquinoline in acetone added to it in sufficient amount to precipitate the uranium and the impurities present in the latter. The precipitate is coagulated by boiling the solution for 3-5 minutes the precipitate is then filtered off and washed with hot water. The filtrate and wash liquors are collected in a separating funnel. Excess 8-hydroxyquinoline and traces of metals remaining in solution are extracted by means of five small portions (10-15 ml) of chloroform. The aqueous phase is filtered in order to remove drops of chloroform. The solution obtained, or an aliquot of it, after adjusting the pH the requisite value with ammonia, is placed in a 50 ml standard flask. To this flask is added 1 ml of a 0.1% solution of eriochrome black T in methanol and the volume made up to the mark; the solution is carefully mixed. The optical density of the solution is measured at 250 mμ with respect to distilled water as reference solution.

The calibration curve is constructed by taking 10-15 samples of a standard $MgSO_4$ solution covering the magnesium concentration range from 1γ to 30 γ, and diluting them to 25-30 ml; the pH is then adjusted and the solutions transferred to 50 ml standard flasks; 1 ml of the dye solution is added to each of the flasks and the volumes made up to the mark. After mixing, the optical density of the solutions is measured and the results plotted on a graph of "optical density" against " magnesium concentration".

The table contains the results for several determinations of magnesium in pure uranium and in uranium containing impurities.

The method permits determination of 0.005% (and higher) of magnesium in uranium with a relative error of not more than ± 3%. Determination can be carried out in hydrochloric, nitric, sulfuric, or acetic acid media. Small amounts of phosphate ions do not interfere (not more than 20 times the amount of magnesium present).

When the optical density is measured on a FÉK-M colorimeter with a green filter the experimental error does not exceed ± 5%.

SUMMARY

A method is described for the spectrophotometric determination of small amounts of magnesium in uranium by means of eriochrome black T. The composition of the colored compound of magnesium with eriochrome black T has been studied.

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TITRIMETRIC DETERMINATION OF MOBILE ALUMINUM IN SOILS

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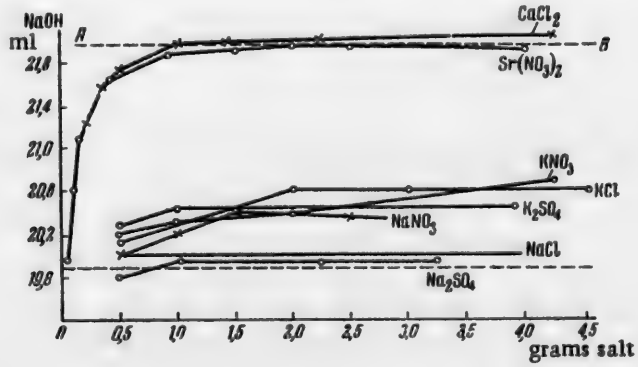
The most often used for determining aluminum and acid in salt extracts of soil is that of Sokolov [1]. This method consists in titrating free acid plus aluminum with alkali, in one aliquot of the solution, the aliquot being heated to the boil, and titration being carried through to the phenolphthalein endpoint; in another aliquot of the same extract the aluminum is complexed with sodium fluoride and the free acid titrated. Aluminum is determined by difference.

The method has a number of disadvantages, namely: during the first titration aluminum hydroxide is precipitated, but formation of basic salts is also possible; the precipitate can adsorb alkali; the presence of a precipitate complicates observation of the titration endpoint. As a result, the method gives high results for aluminum and results with poor reproducibility.

In view of these disadvantages of Sokolov's method we have adopted a titrimetric method of determining aluminum suggested by Pavlinova [2]. The method is based on the capacity of aluminum salts to react with alkali metal tartrates with the liberation of an equivalent amount of acid which is titrated to the phenophthalein endpoint. When this technique is used the solution remains clear right up to the endpoint. The endpoint is more distinct in the presence of foreign salts. In the absence of foreign salts the solution acquires a rose color up to the equivalence point and the results are low.

The effect of the salts of the alkali and alkaline-earth metals is shown in the diagram.



The dotted line AB in the diagram shows the theoretical amount of alkali. The curves obtained in the presence of $CaCl_2$ and Sr $(NO_3)_2$ almost agree with the theoretical straight line for solutions containing from 2% to 7% of $CaCl_2$ or not less than 5% $Cr(NO_3)_2$.

The reaction proceeds according to the following equation

$$4\,AlCl_3 + 3\,K_2C_4H_4O_6 + 4\,H_2O = K_6Al_4(C_4H_2O_6)_3\,O_2(OH)_2 + 12\,HCl.$$

The intercomplex compound which aluminum forms with tartrate, presumably, partially hydrolyzes with formation of KOH; $CaCl_2$ is therefore added to suppress the hydrolysis.

When the test solution contains free acid the latter is titrated with the aluminum. The free acid is determined by adding 10 ml of a 10% solution of potassium oxalate, neutralized beforehand to phenol red, to the extract, and the acid titrated with alkali using the same indicator. The difference in the amount of alkali used for the first and second titrations corresponds to the amount of mobile aluminum, since aluminum, on reacting with tartrates liberates 3 g. equivalents of acid, then 1 ml of 0.1 N alkali corresponds to 0.009 g aluminum.

Preliminary experimental work led to the development of the following method for determining aluminum. To 80 g of soil is added 200 ml of 1 N KCl solution and the whole agitated on a shaker; the mixture is then filtered. The free acid is determined in one aliquot of the filtrate by the method described above, while the total acidity is determined in another. The total acidity is determined by adding 5 ml of a 20% solution of potassium sodium tartrate, neutralized to phenolphthalein, to 25-100 ml of the soil extract, and the mixture titrated with 0.5 N alkali to a distinct red color; 40% $CaCl_2$ solution is then added in such an amount that the final concentration of $CaCl_2$ in the total volume is about 3%; this solution is titrated slowly, dropwise, until a rose color is reached, making sure that the turbidity which develops after the addition of each drop dissolves before adding the next drop. The percentage content of aluminum is calculated by means of the formula

$$Al = \frac{(V - V_2) \cdot N \cdot 0{,}009 \cdot 200 \cdot 100}{80\, V_2},$$

where V is the volume of alkali used for neutralizing the total acidity; V_1 is the volume of alkali used for titrating the free acidity; V_2 is the volume of extract taken for titration; and N is the normality of the alkali.

In order to check the proposed method, aluminum was determined in the same extracts by the suggested tartrate method, and by either a gravimetric method, or a hydroxyquinoline method with a titrimetric finish, and all the results compared with those obtained by Sokolov's method. During the gravimetric determinations aluminum hydroxide was precipitated with ammonium sulfate in the presence of ammonium chloride, since, according to Lyass'er's results [3], the temperature at which aluminum hydroxide is dehydrated depends on the method of precipitation, and in the given instance is equal to 414°, while during precipitation with ammonia the temperature is 1100°.

Small amount of iron and manganese were determined photometrically. Since these metals also liberated acid from tartrates, the volume of alkali used up in neutralizing the acid liberated by these metals was calculated, bearing in mind that iron liberated three equivalents and manganese one equivalent of acid. The results obtained are given in the table.

No. of extract	NaOH 0.004347 N used, ml	Amt. of alkali equiv. to Fe+Mn, ml	Al found, %				
			by free acid, ml	by tartrate method, ml	gravimetrically	hydroxyquinoline method	Sokolov's method
1	8,80; 8,75	0,055	0,075	0,0340	0,0338	—	0,0360
2	12,60; 12,55	0,145	0,175	0,0479	0,0479	—	—
3	2,90; 2,90	0,052	0,100	0,0107	0,0101	0,0103	0,0135
4	2,13; 2,10	—	0,202	0,0075	—	0,0076	—
5	2,23; 2,15	—	0,220	0,0038	—	0,0039	—
6	8,02	—	0,280	0,0151	—	0,0146	—
7	1,220	—	0,418	0,0008	—	0,0008	—
8	1,412; 1,388	—	0,260	0,0022	—	0,0019	0,0029

Notes. In Expts, Nos. 1-4, 25 ml of soil extract was taken, while in Nos. 5, 6, and 8, 50 ml was taken, and in No. 7, 100 ml; in all experiments 5 ml of 20% tartrate, 10 ml of oxalate, and from 3 to 10 ml of 40% $CaCl_2$ were added. The free acid and aluminum in experiments No. 7 and 8 were titrated from a microburet.

SUMMARY

A new titrimetric method is suggested for the determination of mobile aluminum in soils. It has been shown that the proposed method is more accurate and more convenient than the generally used method of A. V. Sokolov.

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DETERMINATION OF MICROAMOUNTS OF ARSENIC BY MEANS OF A SOLUTION OF A DIVALENT CHROMIUM SALT.

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A solution of a divalent chromium salt was used for the first time for a reducing quinquevalent arsenic ions to the elemental (metallic) state by Shat'ko in 1938 during the development of a method for determining 0.26-45% of As in various minerals [1]. In subsequent work a solution of divalent chromium salt was used for determination of 0.1-0.01% of As in ores, casts, and steels, in zinc white, bunker dust, and zinc containing agglomerates [2], in salvarsan preparations and in urine [3] , in tin [4], and in other materials of industrial and sanitary-hygienic importance. The methods developed required large samples (5-10 g), since the sensitivity amounted to 0.39 mg in 100-200 ml of test solution [5].

Our object was to develop a technique for the accurate determination of less than 0.4 mg of arsenic. Small amounts of arsenic are usually isolated by means of ferric hydroxide[6,7] or manganese dioxide [8] used as collectors. In our method the collector used was copper metal produced during reduction with divalent chromium. Divalent copper is quantitatively reduced by Cr^{2+} ion to the elemental (metallic) state in neutral media [1]. Quinquevalent arsenic ions are reduced by Cr^{2+} ions to elemental arsenic in a strongly acid solution (30-40% by volume of HCl sp. gr. 1.19). Under these conditions copper ions remain in solution. Experiments showed that copper is not completely reduced in acid solutions; however, it is reduced in sufficient amount to trap the arsenic precipitate which has been reduced to the elemental state. Copper is then removed from the arsenic by means of ferric ammonium alum. Determination of elemental arsenic can be finished off gravimetrically, photometrically or titrimetrically.

When the gravimetric finish of Zhivanovich was used [9], filtration washing of the precipitated elemental metallic arsenic, and its separation from copper was carried out in a No. 4 Schott crucible. The arsenic remaining was washed with a solution of ammonium chloride and then with water saturated with carbon dioxide, and dried at 105° to constant weight. During determination of 2.2 mg of arsenic by this method, the following results were obtained 2.8, 2.4, 2.2, 2.0, 2.6, and 1.6 mg. The original solution of sodium hydrogen arsenate was standardized gravimetrically by Levol's method [10] and by means of Cr^{2+}[5]. Thus, satisfactory results can be obtained for the determination of down to 2 mg of arsenic in 100 ml. For lower arsenic contents we could not get satisfactory results.

For photometric determination, the arsenic in an elemental state (after separation from copper) was dissolved in sulfuric acid in the presence of hydrogen peroxide. Glucose was used as a reducing agent. During determination of 0.094 mg of As photometrically, the following values were obtained 0.160, 0.112, and 0.096 mg As.

Photometric methods [7,8,11] based on formation of molybdenum blue during the reduction of heteropolyacids are applicable to pure solutions obtained after removal of arsenic from other elements: phosphorus, silicon, boron, germanium, tin, zirconium, cerium, thorium, and other elements also form heteropolyacids, which, on reduction give a blue color.

For the titrimetric method of determining arsenic reduced by divalent chromium to the elemental state, 0.01 N I_2 and 0.01 N $Na_2S_2O_3$ were used as standard solutions. Titrations were carried out with the aid of a microburet. The results obtained are given in the table.

Determination of Arsenic (Elemental) by a Titrimetric Method

As, mg		As, mg	
taken	found	taken	found
0,094	0,114	0,26	0,26
0,094	0,100	0,26	0,28
0,094	0,110	0,26	0,27
0,094	0,110	0,02	0,03
0,094	0,113	0,04	0,03
0,094	0,114	0,02	0,02
0,094	0,110	0,02	0,01
0,26	0,27	0,04	0,04
0,26	0,27	0,02	0,02

For determination of microamounts of arsenic (of the order of 0.02 mg) in solution, the following technique can be recommended :

The test solution is evaporated on a water bath to a volume of 10-20 ml, and 3-5 ml of HCl (sp. gr. 1.19) and 2 ml of $CuSO_4$ (about 0.01 g Cu) added. CO_2 is bubbled through the solution and 7-10 ml of $CrCl_2$ (about 0.5 N $CrCl_2$) or $CrSO_4$ added, the whole is then heated to the boil in a current of CO_2 and boiled for 2-3 minutes. The precipitate is washed 2-3 times with a 2% solution of NH_4Cl, and the copper brought into solution by oxidizing with a solution of ferric ammonium alum (10 ml of a 40% solution). The metallic arsenic remaining on the filter is washed 2-3 times with HCl (1:4) and then 2% NH_4Cl to a pH of 3.7 (methyl orange indicator); the arsenic is finally determined iodometrically as described in [4,5].

The method developed was checked on standard samples of bronze and brass. 0.5-2 g of bronze or brass was dissolved in nitric acid (sp.gr. 1.4) and 10-20 ml of sulfuric acid (1:1) added to convert nitrates into sulfates (evaporation to the appearance of white fumes). After cooling, the dry residue was dissolved in distilled water and quantitatively transferred to a 150 ml flask. The solution was neutralized with sodium carbonate until no more CO_2 was liberated; twice its volume of about 0.5 N $CrCl_2$ solution was then added and the whole boiled for 3 minutes; the mixture was filtered through a fine filter (white band paper can be used) and the precipitate washed 2-3 times with 2% NH_4Cl, 10-20 ml of a 40% solution of ferric ammonium alum was finally added. The arsenic after its separation from copper, was washed 2-3 times with HCl (1:1) and then with 2% NH_4Cl to a pH of 3.75. The filter and precipitate were transferred to a flask, and 5 ml of 0.01 N I_2 and 3 ml of 2% $NaHCO_3$ added (the flask was covered with a watch glass), the solution was finally titrated after 15 minutes with $Na_2S_2O_3$.

For brass containing 0.002% As the following values were obtained: 0.002, 0.0016, 0.0015, and 0.0015 % As.

Antimony, lead, and the other components of bronze and brass do not interfere with the arsenic determination. No cupric sulfate is added for the determination of arsenic in bronze and brass.

The method gives accurate results, demands less time than other methods, and can be used for solving both industrial and sanitary-hygienic problems.

SUMMARY

A method has been developed for isolating microamounts of arsenic by means of a divalent chromium solution, using freshly precipitated (reduced by Cr^{2+} ions) metallic copper as a collector. Copper is removed from the arsenic by means of a solution of ferric ammonium alum. The arsenic which is left (in the elemental state) is then determined iodometrically. The sensitivity of the method is 0.02 mg of As in 100-200 ml. The method has been checked on standard samples of bronze and brass.

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A SIMPLIFIED SPECTROPHOTOMETRIC METHOD OF DETERMINING ORGANIC COMPOUNDS BY MEANS OF THEIR ABSORPTION IN THE NEAR INFRARED

Ts. N. Roginskaya and A. I. Finkel'shtein

Absorption spectra in the near infrared have found application in recent years for solving analytical problems, and for solving problems connected with the determination of the structure of materials [1,2]. In addition to precision spectrophotometric methods in the near infrared, simplified absorptiometric methods involving the use of light filters [3] for isolating the necessary spectral region, have also been used. The possibility is demonstrated in the present article of carrying out an absorptiometric analysis of certain mixtures of organic components which differ comparatively little from each other in their molecular structure.

The apparatus which is schematically shown in Fig. 1 was assembled for carrying out the analysis. In contrast to the usual schemes, we introduced the constant resistances R_1 and R_2, which facilitate measurement for low optical densities. FÉSS-U10 [4] silver sulfide photoelements were used for receiving the radiation. The measurement technique was the same as that used during the work with two-arm photocolorimeters. The cells used for working with organic liquids were made from glass tubes 30 mm in diameter and 200 mm long. These tubes had a side tube in the middle with a ground glass stopper. To the ground faces of the cells, windows were fastened by means of copper tightening washers fitted onto the cell by means of a cement made of glycerol and litharge. This same cement was used for smearing the faces of the cell before fitting on the windows. Cells made in this way proved to be sufficiently stable and suitable for work with the mixtures described below. The light filter used was the copper complex of monoethanolamine [3]. The concentration of the colored complex was chosen empirically so that at the maximum transmission of the light filter, it gave the highest concentration sensitivity. The following light filter answered these requirements most closely: 3.5 mg $CuSO_4 \cdot 5H_2O$ was dissolved in 50 ml of water and 10 ml of monoethanolamine added. The absorption spectrum obtained on the UM-2 monochromator with a germanium photoelement is shown in Fig. 2. The cells for the light filter were made from organic glass. The thickness of the absorbing layer was 10 mm. Calibration curves were used in each case for the determinations

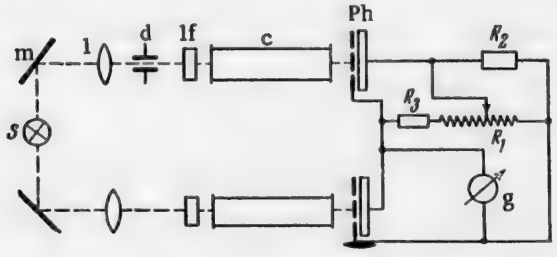

Fig. 1. Schematic diagram of the apparatus: S) Light source (incandescent lamp 6b, 21 c.p.); m) mirror; *l*) lens (F=10 cm); d) diaphragm; *l* f) light-filter (monoethanolamine complex of copper); c) cell; ph) photoelement; (FÉSS-U10); R_1 =75 ohms; R_2=50 ohms; R_3 = 750 ohms; G) galvanometer type GMP. GMP.

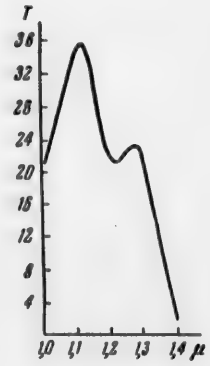

Fig. 2. Absorption spectrum of the light-filter (ordinate T,% abscissa λ, μ).

TABLE 1

Chlorex, %		Error, % %	
taken	found	absolute	relative
50,0	49,0	—1,0	2,0
40,0	37,5	—2,5	6,25
25,0	23,5	—1,5	6,0
15,0	14,5	—0,5	3,3
10,0	10,05	+0,5	5,5
5,0	4,8	—0,2	4,0

TABLE 2

Water, %		Error, % %	
taken	found	absolute	relative
4,05	4,10	0,05	1,23
5,70	5,80	0,10	1,75
7,47	7,50	0,03	0,40
12,01	12,0	0,01	0,83

(Fig. 3). In a previous article [5] we described a spectrophotometric method of analyzing a mixture of chlorex (β,β' dichlorodiethyl ether) and dichloroethane on the basis of their absorption spectra in the ultraviolet and infrared. In the same article we gave the absorption spectra of chlorex and dichloroethane in the near infrared, and indicated the possibility of developing a method which uses this region of the spectrum. Experimental work completely confirmed these suggestions. Table 1 contains the results for the analysis of synthetic mixtures. The mean relative error of 15 determinations of chlorex within the concentration range 5 to 40%, was about 7%. Such an error is quite acceptable for production control. Under the same conditions, similar results were obtained for the determination of water in isopropanol (Table 2). The sensitivity threshold of the method in this case proved to be about 1%. The highest accuracy was found in the limits 1-10% when a cell 200 mm long was used. The mean relative error of 10 determinations was about 2.5%, which corresponds to the accuracy of the usual photocolorimetric methods of analysis. Cyclohexanol in cyclohexanone (Table 3) was also determined. In this case the threshold sensitivity was about 5%, the mean arithmetic error was about 4%. An analysis took about 5-10 minutes in all three cases.

TABLE 3

Cyclohexanol %		Error, %	
taken	found	absolute	relative
4,95	5,5	+0,55	11,1
10,0	9,9	—0,10	1,0
19,9	22,0	+2,1	10,5
34,3	35,0	+0,7	2,04
49,7	51	+1,3	2,8

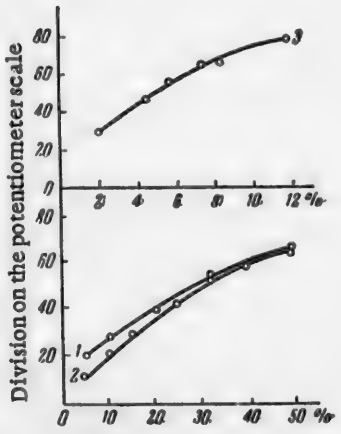

Fig. 3. Calibration curves for various determinations: 1) Chlorex in dichloroethane; 2) cyclohexanol in cyclohexanone; 3) water in isopropanol.

The results obtained show that even in the case where compounds with similar absorption spectra are analyzed, simplified methods of analysis in the near infrared can give satisfactory results.

SUMMARY

It has been demonstrated that it is possible to analyze mixtures of organic compounds with similar absorption spectra in the 1-2 μ region by means of a simplified spectrophotometric method.

Taking as examples the determination of chlorex in dichloroethane water in isopropanol, and cyclohexanol in cyclohexanone, the potentialities of simplified absorptiometric methods for control production of organic chemicals has been demonstrated.

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DETECTION AND DETERMINATION OF RHENIUM

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Pottassium perrhenate in the presence of hydrochloric acid, divalent tin, and sulfite, gives a colored compound. The conditions for carrying out the reaction have been studied on a FÉK-M photocolorimeter using supplementary light-filters whose characteristics are similar to those of Ilford light filters [1].

As preliminary experiments showed, color developments depends on acid concentration. From Table 1 it is clear that the est results are obtained for a concentration of about 4 g-equivalents/liter of hydrochloric acid (taking into account the acid contained in the stannous chloride solution). Further increases in acidity lead to rapid development of turbidity in the solution as a result of the deposition of the compound $Sn_5O_5Cl_{10}$, which is insoluble in hydrochloric acid [2]. In the presence of sulfuric acid, hydrolysis takes place more intensely. Oxalic, tartaric, and citric acids are used for slowing hydrolysis of tin compounds. The best results were obtained in our case with citrate ions at a concentration of 0.04 mole/liter. The optimum concentration of stannous chloride was found to be 0.22 mole/liter, while that for sodium sulfide was 0.04 mole/liter. 15-20 minutes was found to be sufficient for complete color development. The rate with which the color develops, and its intensity, increase on addition of alcohol. Nevertheless, in the presence of 5 ml of ethanol a turbidity develops in 10-13 minutes.

The color intensity depends on the order in which the reagents are added. The optimum color is observed when the following order is adopted: to a 25 ml flask containing the solution of the rhenium compound is added 10 ml of hydrochloric acid (2:1) and 2 ml. of 0.5 M sodium citrate, and the mixture cooled, 1 ml of 1 M sodium sulfite is then added, followed by 1 ml of a 5% solution of stannous chloride, and the volume made up to the mark with distilled water. The optical density is measured after 20 minutes. Solutions of stannous chloride and sodium sulfite change in air accordingly; they be protected from the air or should be prepared freshly every day.

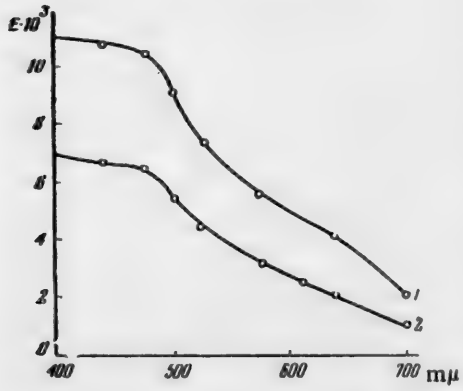

Fig. 1. Absorption curves of the rhenium complex: 1) in aqueous solution; 2) in the isoamyl alcohol layer.

Maximum absorption by the Re complex is observed in the ultraviolet (Fig. 1). The molar extinction coefficient is 1.1×10^4. Solutions conform to Beer's law down to concentrations of 8γ of rhenium/ml (Fig. 2). The relative experimental error for the photometric determination of rhenium does not exceed 7% (Table 2).

The presence of vanadium compounds to the extent of 0.2 mg. and of nitrate ions to the extent of 0.1 mole/liter does not interfere with rhenium determination. Ions with an intrinsic color (nickel, chromium, and cobalt) increase the color intensity. Molybdates and tungstates also interfere.

A study of the possibility of extracting the rhenium complex with benzene, toluene, chloroform, isoamyl acetate, diethyl ether, butanol, and isoamyl alcohols. The colored rhenium compound was found to be extracted with butanol and isoamyl alcohol. The color is stable for one hour in the alcohol layer. The absorption curve of the extract is shown in Fig. 1.

TABLE 1

Effect of Acidity on the Color of the Solution (Re-93γ ; 1 ml of 1M Na_2SO_3 2 ml of 0.5 M sodium citrate; 1 ml of $SnCl_2$; volume -25 ml; time 20 min.)

Acid concentration, g. equivalent/ liter	Relative density
1,4	0,03
2,0	0,15
2,8	0,85
4,0	0,97
4,6	Becomes turbid after 14 min
5,4	Becomes turbid after 6 min

TABLE 2

Photometric Determination of Rhenium with Sulfite

Rhenium, γ		Error, γ
taken	found	
2,8	2,8	0,0
5,6	5,8	+0,2
8,4	7,9	−0,5
13,0	13,9	−0,9
18,6	18,2	−0,4
27,9	27,0	−0,9
55,8	54,7	−1,1
74,4	74,4	0,0
111,6	109,6	−2,0

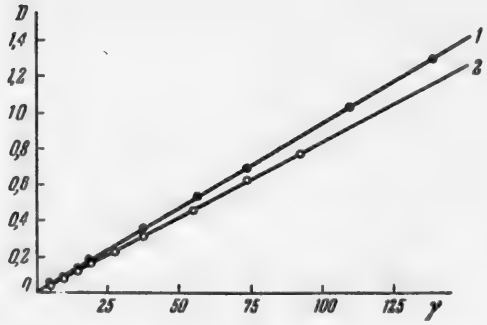

Fig. 2. Conformity to Beer's law: 1) aqueous solution, volume 25 ml; 2) isoamyl alcohol layer volume 11 ml; a light filter with transmission at 400 mμ was used.

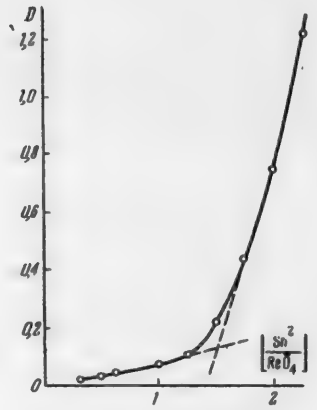

Fig. 3. Optical density of the solutions for variable stannous chloride concentrations.

The molar extinction coefficient is less in the alcohol layer than in the aqueous layer, and amounts to 6.9×10^3. Thus, extraction with isoamyl alcohol permits the sensitivity of the method to be increased only by transferring the sulfite complex into the alcohol layer which is smaller in volume. The extract in isoamyl alcohol conforms to Beer's law (Fig. 2).

In order to detect rhenium, its solution contained in a 100 ml separatory funnel is prepared as described above. After 20 minutes, 11 ml of isoamyl alcohol is added. The whole is shaken for 30 seconds, and the layers allowed to separate; the lower aqueous layer is rejected. The colored alcoholic layer is often turbid because of the formation of a stable emulsion. Accordingly, it is poured through a dry filter paper 3 cm in diameter into a 30 mm cell. Photometric measurements are made with a light-filter whose transmission is located at 400 mμ. Isoamyl alcohol is used as the reference solution.

Rhenium can be detected by adding 2 ml of concentrated hydrochloric acid to a test tube containing 2 ml of a test solution which contains perrhenate; the whole is thoroughly mixed and 0.25 ml of 1 M sodium sulfite and 0.25 ml of a 5μ solution of stannous chloride dissolved in concentrated hydrochloric acid added. The color develops with time and is compared with distilled water after 3-5 minutes. After standing for 10-15 minutes, the solution becomes turbid. This method permits detection of as little as 0.5γ rhenium. Those elements which interfere during the quantitative determination also interfere here.

The sign of the charge of the ion of the rhenium complex formed was determined by ion exchange chromatography. For this purpose the colored solution was passed through a column containing the cation exchange resin SBS in the H-form. The filtrate obtained was colored. On passing the test solution through a column filled with the anion exchange resin TN in the OH-, Cl-, and SO_4-forms, the ion exchange resins became colored while the filtrate obtained was colorless. When the anion exchange columns were subsequently elute with hydrochloric and sulfuric acids, the resin was decolorized and the eluate was colored. Thus, the behavior of the complex on ion exchange resins indicates that its colored part is the anion.

The valence of rhenium was determined photometrically [3]. Stannous chloride solution was prepared by dissolving tin metal in concentrated hydrochloric acid in a hydrogen atmosphere. Potassium perrhenate, chemically pure grade, was dissolved in distilled water on heating. In order to get the colored solution, the amounts of rhenium and stannous chloride taken were calculated, and the concentrations of the acid, sulfite, and citrate were the same for the determination of rhenium. The break on the curve in Fig. 3 is located at a point corresponding to a ratio of $[Sn^{2+}]:[ReO_4^-] = 1.5$. The oxidation – reduction process which occurs during formation of the complex compound, can be expressed by the scheme

$$2ReO_4^- + 3\,Sn^{2+} + 12H^+ = 2ReO^{2+} + 3\,Sn^{4+} + 6H_2O$$

Consequently, rhenium is quadrivalent in this complex.

SUMMARY

A new reaction for rhenium has been developed. Conditions have been developed for the quantitative and qualitative determination of rhenium. It has been shown that rhenium is quadrivalent in the rhenium sulfite complex, and that the colored part of the complex is the anion.

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A NEW PHOTOMETRIC METHOD FOR THE DETERMINATION OF NICKEL

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The ammonium salt of purpuric acid — murexide — $C_8H_8N_6O_6H_2O$, which is used for determination of water hardness and for the photometric determination of calcium [1], reacts with nickel salts in a weakly ammoniacal medium and changes its color from purple-red to orange yellow. By means of aqueous murexide it is possible to detect as little as 0.2 γ of nickel in 1 ml of solution at a limiting dilution of $1:5 \times 10^6$.

The reaction is carried out by adding 0.2 ml of 0.5% ammonia solution and 0.05 ml of a 0.02% aqueous solution of murexide to 1 ml of test solution.

Salts of the alkali and alkaline-earth elements, Mo^{VI}, V^V, W^{VI}, Pd^{II}, $Pt^{II,IV}$, Zr^{IV}, Th^{IV}, Nb^V, Ta^V, Au^{III}, Te^{IV}, Se^{IV}, Be, Ag, Cd, AsO_4^{III}, PO_4^{III} and Cu^{II} do not interfere with detection of nickel.

Fe^{II}, Fe^{III}, Co^{II}, Pb^{II}, and Mn^{II} salts do not react with the reagent but large concentrations interfere with the reaction.

Only zinc and magnesium salts react with murexide in a weakly ammoniacal medium, changing its color from purple-red to orange-yellow. The sensitivity of the reaction with zinc is 1γ in 1 ml at a limiting dilution of 1: 1,000,000 while for magnesium the sensitivity is 20γ in 1 ml at a limiting dilution of 1: 50,000. Presumably, zinc and magnesium react with murexide in the same way as nickel, as a result of the similarity in the radii of their ions. A 0.02γ aqueous solution of murexide can be used for the photometric titration of nickel. The color obtained on adding an aqueous solution of murexide to a weakly ammoniacal solution containing nickel in the concentration range 0.2 γ to 5γ in 1 ml of solution, conforms to Beer's law. Excess reagent interferes by virtue of its own color, accordingly, the method of colorimetric titration is used. We have established that 0.2 ml of a 0.02γ aqueous solution of murexide corresponds to 1 γ of nickel.

The colorimetric titration method of determining nickel in steels consists of the following. 0.10-0.20 g of steel is dissolved on boiling in sulfuric acid (1: 9), 1 ml of hydrogen peroxide is then added in order to oxidize Fe^{II} to Fe^{III}; the acid solution is neutralized by ammonia, the latter being added until the iron is almost precipitated (pH 6.2-6.4). To the weakly acid solution is added 10 ml of 0.5 N zinc sulfate and the whole mixed. 10 ml of 1 N $K_3[Fe(CN)_6]$ is then added and the precipitate of $Zn_3[Fe(CN)_6]_2$ containing all the nickel filtered off [2-3], the precipitate is washed several times with water. To the precipitate on the filter is added excess 5% NaOH in which the $Zn_3[Fe(CN)_6]_2$ dissolved, while traces of iron and nickel in the form of their hydroxides remain on the filter. The sodium hydroxide should be free from carbonate. Iron and nickel hydroxides are dissolved in sulfuric acid (1: 9) and excess acid neutralized with ammonia, the latter being added in excess; the mixture is then boiled. The solution containg the ammoniacal complex of nickel is boiled to remove excess ammonia and collected in a 100 ml standard flask (or in a larger flask in the case of a high nickel content). All these operations are necessary for concentrating traces of nickel and for separating it from the major part of the iron. The volume of the solution of the ammoniacal complex of nickel is made up to the mark with water, the solution is thoroughly mixed and a 10 ml aliquot of the solution used for the photometric titration with murexide. The aliquot is titrated with a 0.02% aqueous solution of murexide to the appearance of an orange-yellow color, and the color compared with a series of standard, titrated solutions of nickel. The series of standard, titrated solutions of nickel are prepared as follows. Into 10 titration tubes with flat bottoms and fitted with ground glass stoppers, are introduced 10 ml lots

TABLE 1

Determination of the Nickel Content of Steel by means of Murexide (0.1 g of steel was taken, the solution was diluted to 100 ml)

Ni content, %	Ni found %	Difference
0,10	0,10	0,00
0,12	0,11	0,01
0,14	0,13	0,01
0,15	0,15	0,00
0,18	0,17	0,01
4,20	4,00	0,20

of nickel standard solutions containing 0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 γ of nickel in 1 ml of solution. To each tube is added 1 ml of a 0.5 % ammonia solution and the whole mixed. After mixing, 1,2,3, 4,5,6,7,8,9, and 10 ml of a 0.2 % aqueous solution of murexide is added to the series of tubes, and the contents of the tubes mixed. Aqueous solutions of murexide are not particularly stable, the intensity of the purple color decreases in the course of 3-5 days; accordingly, the reagent and the series of standard titrated solutions should be prepared on the day they are to be used.

Results for the determination of nickel in steels are given in Table 1.

The method gives good results: the insignificant deviations obtained are quite permissible for a photometric method.

Subsequently, in order to check the method and to establish the effect of low concentrations of cobalt , the following determinations were carried out. 0.10 g of steel whose nickel content had been determined beforehand, was dissolved in sulfuric acid (1: 9), known amounts of nickel and cobalt salts in the form of solutions were then added; the mixture was treated with hydrogen peroxide in order to oxidize Fe^{II} to Fe^{III}, and the procedure outlined above for the determination of nickel in steel subsequently followed.

It is clear from Table 2 that for ratios of Ni: Co = 1: 10 the method gives good results.

TABLE 2

Determination of Nickel in the Presence of Cobalt in Steels using Murexide

Ni content, %	Ni added, %	Co added, %	Ratio Ni: Co	Total Ni content, %	Ni found, %	Difference
0,10	0,05	0,5	1: 3	0,15	0,14	0,01
0,12	0,08	1,0	1: 5	0,20	0,19	0,01
0,14	0,06	1,0	1: 5	0,20	0,20	0,00
0,15	0,10	2,5	1: 10	0,25	0,23	0,02
0,18	0,32	5,0	1: 10	0,50	0,50	0,00

SUMMARY

A 0.02% aqueous solution of murexide -ammonium purpurate- $C_8H_8N_6O_6 \cdot H_2O$ reacts with the nickel ammonia complex, and its color changes from purple-red to orange - yellow. The limit of identification is 0.2 γ of nickel in 1 ml of solution at a limiting dilution of 1: 5,000,000.

The color of the solutions conforms to Beer's law. A new colorimetric titration method has been developed for the determination of nickel in steels.

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AMPEROMETRIC DETERMINATION OF COBALT BY AN IODOMETRIC METHOD USING A ROTATING PLATINUM MICROELECTRODE

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Results for the determination of cobalt in ammoniacal media by direct titrationwith ferricyanide are somewhat low because of the partial oxidation of cobalt by dissolved atmospheric oxygen.

An iodometric method for the determination of cobalt in an ammoniacal medium, which was suggested recently, enables correct results to be obtained even in the presence of dissolved atmospheric oxygen [1].

Taking this fact into account, and also bearing in mind the ease with which free iodine is reduced on a platinum electrode, we decided to investigate the possibility of carrying out an iodometric titration of cobalt in an ammoniacal medium, using an amperometric technique for establishing the endpoint. The setup plus the rotating platinum microelectrode have been described before [2].

The concentration of the original solution of chemically pure cobalt sulfate was established by the sulfate method. The working solutions of iodine and sodium arsenite were prepared by taking accurately weighed aliquots of freshly distilled iodine, and chemically pure arsenic oxide.

During a direct amperometric titration of an ammoniacal solution of cobalt with the iodine solution it was established that, in the absence of excess iodine, the reaction between cobalt and iodine proceeds too slowly as a result of which the titration process takes too long. Thus, from a practical point of view, direct titration of cobalt with iodine in the presence of ammonia and ammonium citrate, on the basis of the formation of iodopentamminocobaltinitrite, proved unsuitable. Positive results were obtained, however, during determination of cobalt by titration of excess iodine with sodium arsenite.

Cobalt was determined as follows: a known volume of a standard solution of cobalt was introduced into a 100 ml beaker used as the titration flask, and 25 g of ammonium nitrate added; the solution obtained was then brought up to room temperature. To this solution was then added from a buret a standard iodine solution in such amount that not less than 1-2 ml of standard sodium arsenite would be required for titrating the excess iodine. 5 ml of 18% ammonia solution was next added, followed by sufficient water to bring the final volume of the solution to 40-50 ml. After standing for 5-10 minutes the excess iodine was titrated with the standard sodium arsenite added from a 5 ml microburet, at a cathodic polarization of the microelectrode of 0.1 volt.

During the initial stages of the titration, the sodium arsenite was added in large portions without measuring the current. The current was only measured at a high galvanometer sensitivity when most of the iodine had been reduced. From this point onward the reagent was added dropwise. Adoption of such a technique ensured that a clearly defined titration curve with a steep left branch was obtained. Titration did not take more than 2-3 minutes.

As Table 1 shows, the titration results are sufficiently accurate and show good reproducibility. The smallest concentration of cobalt was approximately 0.01 mg/ml.

Dissolved oxygen has no effect on the accuracy of the determination.

Sulfate, nitrate, acetate, tartrate, and chromate do not interfere with titration of cobalt even when the molar concentration of these anions exceeds that of cobalt 100 times (Table 2).

TABLE 1

Determination of Various Amounts of Cobalt (average of 4-5 parallel determinations)

Cobalt taken, mg	Cobalt found, mg	Mean dev. of one determ. from mean		Dev. of mean value found from taken	
		in mg	in %	in mg	in %
51,38	51,84	0,02	0,04	0,46	0,89
25,44	25,45	0,11	0,43	0,01	0,04
20,50	20,50	0,04	0,19	0,00	0,00
15,36	15,38	0,05	0,31	0,02	0,13
10,28	10,19	0,01	0,14	0,09	0,87
5,13	5,14	0,03	0,43	0,01	0,19
2,54	2,54	0,01	0,47	0,00	0,00
1,54	1,55	0,01	0,80	0,01	0,64
1,03	1,04	0,01	0,72	0,01	0,97
0,51	0,48	0,02	4,16	0,03	6,00

TABLE 2

Effect of Foreign Ions on the Results of Titrating 20 and 50 mg of Cobalt (average of 3 cobalt determinations)

Foreign salt	Mol. ratio of foreign ion to cobalt	Cobalt found, mg	Max. dev. from mean, %	Dev. of means found from taken	
				in mg	in %
Effect of anions					
Ammonium sulfate	100	20,53	0,10	0,02	0,10
Ammonium citrate	100	20,54	0,14	0,04	0,19
Ammonium tartrate	100	20,44	0,34	0,06	0,29
Ammonium acetate	100	20,61	0,19	0,11	0,53
Ammonium nitrate	1000	20,49	0,39	0,01	0,05
Ammonium chloride	1	19,91	0,42	0,59	2,87
Ditto	0,01	20,44	0,14	0,06	0,29
Potassium chromate	50	20,55	0,53	0,05	0,24
Effect of cations					
Calcium nitrate	50	20,62	0,24	0,12	0,58
Strontium nitrate	50	20,60	0,43	0,10	0,48
Barium nitrate	50	20,69	0,14	0,19	0,92
Magnesium sulfate	10	20,67	0,10	0,17	0,82
Ditto	1	20,46	0,05	0,04	0,19
Zinc nitrate	100	20,48	0,14	0,02	0,10
Aluminum nitrate	20	20,30	0,20	0,20	0,97
Ditto	40	20,04	0,20	0,46	2,23
Ferric sulfate (III)	10	20,77	0,24	0,27	1,31
Ditto	5	20,65	0,19	0,15	0,73
Nickel nitrate	10	20,98	0,38	0,48	2,34
Ditto	5	20,60	0,14	0,10	0,48
Cadmium acetate	20	20,73	0,19	0,23	1,12
Ditto	10	20,64	0,10	0,14	0,67
Copper nitrate	15	20,70	0,24	0,20	0,97
Ditto	10	20,61	0,19	0,11	0,53
Lead nitrate	40	20,26	0,29	0,24	1,17
Ditto	20	20,42	0,19	0,08	0,39
Bismuth nitrate	10	20,80	0,05	0,30	1,46
Ditto	5	20,46	0,24	0,04	0,14
Chromium nitrate	1	19,88	0,10	0,62	3,02

Chloride ions interfere; they depress the results; chlorides are only tolerated in small amounts (of the order of 1% of the cobalt). Presumably, chloride ions enter into the inner sphere of the complex instead of iodide ions.

Calcium, strontium, barium, zinc, magnesium, aluminum, trivalent iron, nickel, cadmium, copper, lead,

bismuth, even in large amounts do not interfere. During titration, aluminum, iron, and bismuth ions were kept in solution by addition of ammonium citrate, while excess potassium iodide was added to keep lead in solution. Cr^{3+} ions interfere; they were accordingly oxidized to chromate. Divalent manganese, even in small amounts, interferes. Manganese was therefore oxidized by potassium permanganate in an acid medium in the presence of fluoride ions, using the amperometric technique for establishing the endpoint. To the cobalt solution to be titrated and containing various amounts of manganese, was added 4 ml of 2 M sulfuric acid, and 20-25 g of ammonium fluoride, after which the manganese was oxidized with permanganate, the latter being added dropwise, until the current arising from the oxidation of Mn^{2+} ion on the microelectrode was kept at +0.6 volt. After the manganese had been oxidized, the cobalt was determined in the solution thus obtained by the method described above. In this way it was found possible to get sufficiently accurate results, as long as the manganese concentration did not exceed that of the cobalt.

SUMMARY

It has been shown that it is possible to titrate cobalt amperometrically by an iodometric method using a rotating platinum microelectrode. The method gives reasonably accurate results for the determination of cobalt alone, and for its determination in the presence of many foreign ions. One of the advantages of the method is that dissolved atmospheric oxygen does not interfere.

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DETERMINATION OF NaOH, Na_2CO_3, and $NaHCO_3$ IN THEIR MIXTURES BY AN ELECTROMETRIC NONCOMPENSATING METHOD*

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In a previous paper [1] we published examples of the application of an electrometric noncompensating method of titrating acid mixtures containing nitric, sulfuric, phosphoric, and chromic acids such mixtures being difficult to deal with from an analytical point of view. The present article is devoted to the use of an electrometric noncompensating method for titrating another mixtures which is interesting from the analytical point of view, namely a mixture of NaOH, Na_2CO_3, and $NaHCO_3$.

Titration of solutions of these alkalis is carried out by means of a tungsten electrode paired up with a copper sulfate electrode which serves as the reference electrode. Its construction has been described in a previous article [2].

The indicator electrode (Fig. 1) is made from a tungsten wire or spiral connected by means of tin to a copper wire. The tungsten wire 1 whose thickness is not less than 0.2 mm is fitted into a small sleeve filled with molten tin 3. The sleeve is soldered to a copper wire 4. The tungsten wire should be at least 3.5 cm long. The copper wire is about 15 cm long while its thickness is 2-3 mm. After the tin has cooled down the electrode is firmly fastened to the copper wire. The point at which the tungsten wire is fixed, and all the sleeve, is covered with any type of lacquer or with BF-2 universal glue.

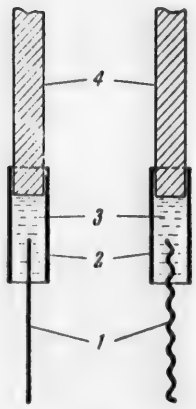

Fig. 1. Contructional details of the tungsten electrode.

The procedure for electrometric noncompensating titration and the arrangement of the electrodes in the solution being titrated have been described previously [1].

Quinhydrone, antimony, molybdenum, and tantalum electrodes were tested in the course of the work described here as indicator electrodes for titrating the solutions of the alkali mixtures, in addition to the tungsten electrode. The best electrodes proved to be the tungsten and molybdenum electrodes. Such widely used electrodes as the antimony and quinhydrone electrodes were found to be less sensitive to changes in H^+ ion concentration than the tungsten electrode.

The relatively high sensistivity of the tungsten electrode to hydrogen ions has been noted before; Kolthoff and Furman [3] referring to the work of Bayliss, point out that the potential of the tungsten electrode changes by 90 millivolts for a change of one in the pH, i. e., it is 90-58 = 32 millivolts greater than the potential of the hydrogen electrode.

The molybdenum and tantalum electrodes are similar in properties to the tungsten electrode, but these electrodes are less sensitive to hydrogen ions than tungsten.

In our work the alkali mixtures were invariably titrated with 0.1 N HCl. The volume of the solution being titrated was always 50 ml. Titration was carried out with an external resistance of R = 5000 ohms.

Determination of NaOH. The titration curve for NaOH is shown in Fig. 2.

* L. E. Sud'bina carried out the experimental work.

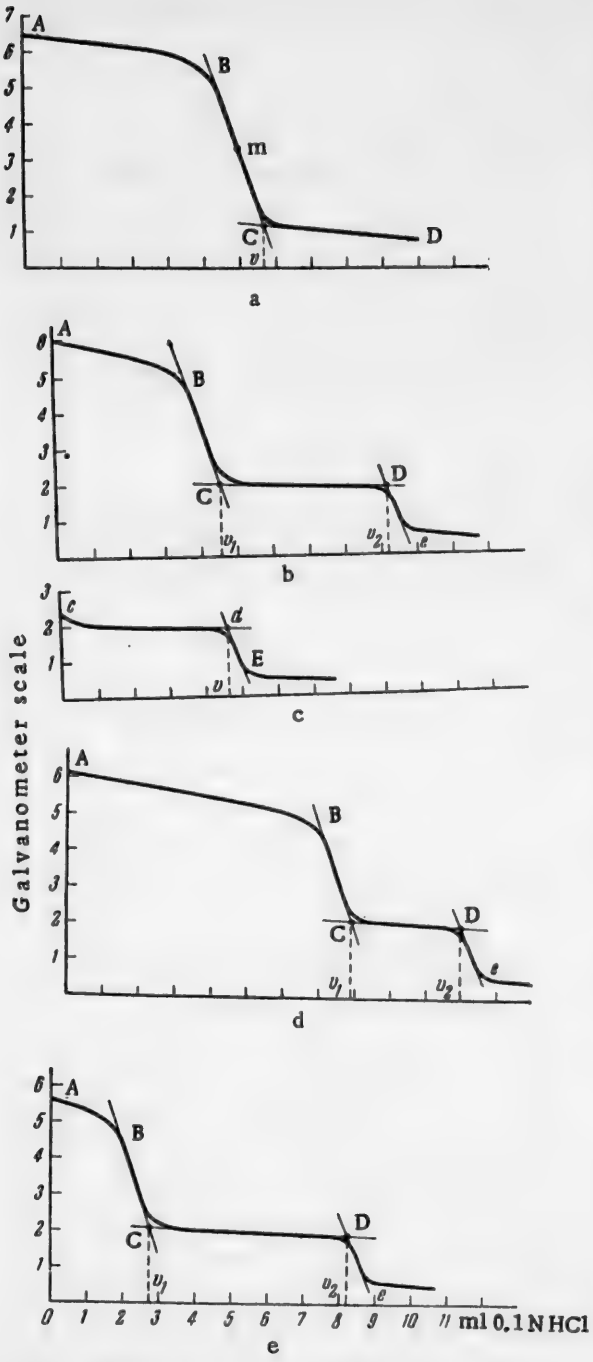

Fig. 2. Titration curves for: a) NaOH; b) Na_2CO_3; c) $NaHCO_3$; d) NaOH + Na_2CO_3; e) Na_2CO_3 + $NaHCO_3$.

During titration of a strong acid by a strong base (and vice versa) by means of a compensating method, the equivalence point on the titration curve corresponds to the break on the curve (point m), at which dE/ dv has a maximum value. In contrast to the compensating method, however, in the electrometric noncompensating method of titrating the equivalence point does not lie at point m, but is somewhat lower. The equivalence point on the curves obtained during noncompensating titration is determined by the intersection of the two tangents as shown in Fig. 2 (point c). The amount of acid used for titrating the NaOH is determined by the projection of point c into the abscissa (point v).

Determination of Na_2CO_3. The titration curve for a solution of Na_2CO_3 is shown in Fig. 2.

The steplike form of the titration curve is explained by the fact that neutralization of sodium carbonate by hydrochloric acid proceeds in two stages:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl.$$

Neutralization of sodium carbonate according to the first equation proceeds along the part abc, while neutralization of the bicarbonate thereby formed proceeds according to cd. At point d decomposition of sodium bicarbonate is complete, after which the potential of the indicator tungsten electrode changes as a result of addition of excess HCl.

The amount of acid used for neutralizing the Na_2CO_3 is determined by point c, or on the abscissa by v_1. The total amount of acid used for neutralizing all the Na_2CO_3 is determined by d, or , on the abscissa by v_2. From this, it follows that the acid used for neutralizing the $NaHCO_3$ will be given by $\Delta v = v_2 - v_1$.

Determination of $NaHCO_3$. The titration curve is shown in Fig. 2c.

Here as in the previous curve (Fig. 2b) the interaction between HCl and $NaHCO_3$ proceeds according to cd on the titration curve. The equivalence point corresponds to point d, or , on the abscissa to v.

Analysis of Mixtures of NaOH and Na_2CO_3. The titration curve for a solution containing both these components is shown in Fig. 2d.

During a titration of this mixture, NaOH is initially neutralized, being the stronger base; Na_2CO_3 is then neutralized, and finally the $NaHCO_3$ formed. abc corresponds to the process of neutralizing total NaOH and half the Na_2CO_3. Titration of the $NaHCO_3$ formed, i. e. the second half of Na_2CO_3, is shown on the curve by cd. Points c and v_1 determine the acid used for titrating total NaOH and half the Na_2CO_3, while points d and v_2 determine the total expenditure of acid for titrating both components of the alkali mixture. From this, it follows that the difference $\Delta v = v_2 - v_1$, equal to section cd, should determine the amount of acid used for titrating the $NaHCO_3$ formed.

Using these relationships, it is possible to find the amount of acid used for titrating both Na_2CO_3 and NaOH. The acid used for titrating Na_2CO_3 should be $v = 2\Delta\ v = 2(v_2 - v_1)$.

While for titrating the NaOH, the acid used for will be given by $v = v_1 - \Delta v$ or

$$v = v_2 - 2(v_2 - v_1) = 2v_1 - v_2 .$$

Analysis of a Mixture of Na_2CO_3 and $NaHCO_3$. The titration curve for a solution containing both these components is shown in Fig. 2e.

Here, as for titration of Na_2CO_3 alone, the part abc represents neutralization of exactly half the Na_2CO_3, while cd represents titration of sodium bicarbonate. Points c and v_1 determine the amount of acid used up for neutralizing half the Na_2CO_3 in solution. cd, or the difference $\Delta v = v_2 - v_1$, determines the amount of acid used for titrating all the $NaHCO_3$, i. e., the $NaHCO_3$ already in solution and that formed from Na_2CO_3. On the basis of these results it is possible to determine the amount of acid used for titrating each component of the mixture indicated.

The acid used for titrating Na_2CO_3 is given by $v = 2v_1$.

The acid used for titrating the $NaHCO_3$ in the mixture is given by $v = v_2 - 2v_1$.

The accuracy of the electrometric noncompensating method for analysis of mixtures of the components indicated lies within the limits ± 0.5 - 1.0 % relative, depending on the sensitivity of the galvanometer, the value chosen for the external resistance R, and the accuracy of the construction of the titration curves.

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DETERMINATION OF THE GYPSUM CONTENT OF CEMENT BY MEANS OF CATION-EXCHANGE RESINS

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The methods currently used in cement factories for the determination of the gypsum content of cement [1,2] are not satisfactory. A method we have developed which is based on the use of cation exchange resins is characterized by the ease with which it can be carried out, by high accuracy, and speed (30-35 minutes).

Methods are already known [3-6] for the determination of the sulfate content of solutions by means of cation exchange resins.

The major difficulty in the determination of the gypsum content of cement is the choice of a suitable solvent which would be capable of getting all the cement sulfates into solution, touching as little as possible of the remaining components in the process, so that the extract does not contain too many cations.

The gypsum in the cement* was first of all extracted by means of distilled water: 0.5 g of cement was treated with 100 ml of water for 10 minutes. The water extract contained calcium in the form of sulfate and hydroxide, alkali metal sulfates, a very small amount of the aluminum in the form of aluminates, and soluble silicic acid. Nevertheless, only 0.5% SO_3 was obtained from several examples of cement extracted in this way.

Better results were obtained on using a more agressive solvent 5% boric acid solution. On treating 0.5 g of cement with 25 ml of boric acid, 30-50% of the aliquot dissolved, while the SO_3 content of the insoluble residue dropped to 0.05-0.07% and did not exceed 0.15%; this was fully permissible.

In order to decrease the decomposition of clinker materials we chose a combined method of extracting the sulfates: aliquots of material were treated with 25 ml of water and the insoluble residue treated on the filter with a 5% solution of boric acid. When this method was used, 20-30% of the material in the form of sulfates, borates, and silicates of calcium, magnesium, and alkali metals, dissolved. On passing such a solution through a column of cation exchange resin in the hydrogen form the equivalent amount of sulfuric acid, and also of boric and silicic acids were formed.

By titrating the solution obtained with 0.1 N alkali solution using methyl orange as indicator, the gypsum content of cement was determined. Under these conditions boric and silicic acids were not titrated.

To extract 10% and less of the gypsum from the cement it was necessary to treat 0.5 g of sample with 25 ml of distilled water with continuous agitation for 10 minutes. The solution was filtered and the insoluble residue washed initially 2-3 times by decantation, and then washed 3-4 times on the filter with 5% boric acid. The filtrate and wash liquors were passed successively through the resin column at a rate of 3-4 ml per minute; the column was then washed with 50-70 ml water at the same rate, and the total solution, about 100 ml in all, titrated with standard alkali solution using methyl orange as indicator.

The column which was 1 cm in diameter was filled with cation-exchange resin to a height of 17-20 cm.

* Some alkali metal sulfates are found in the clinker part of the cement; these sulfates, usually, as in the given case, are determined together with the sulfate part of the gypsum.

The cation exchange resin was kept overnight in distilled water and then transferred, using water, into the column in which a lump of glass wool had been placed beforehand; a few glass beads were placed on top of the glass wool. There should be no air bubbles among the cation exchange resin grains, otherwise, the exchange rate is depressed. The column prepared in this way was washed 3-4 times with 3 N hydrochloric acid in order to convert the resin into the H-form, the acid was passed through at the rate of 3-4 ml per minute. The column of resin in the H-form was then washed with distilled water until the wash liquors gave a neutral reaction with methyl orange; the test solution was finally passed through.

The method gives fully satisfactory results (table); the deviation does not exceed 0.15% absolute, when compared with the results of the gavimetric method.

5-6 determinations can be carried out without regenerating the resin. It is necessary check for complete absorption of the cations by adding ammonium oxalate to the solution obtained after titrating the last filtrate (after the sixth determination) with alkali. The absence of any precipitate indicates that the result obtained is correct. When a precipitate appears then the column should be regenerated immediately by passing 70-100 ml of 3-4 N hydrochloric acid through it, and washing with distilled water until the washing give no reaction for chloride ions.

Образец	SO_3 content, %				By the gravimetric method	SO_3 content of the insoluble residue, %
	Cation exchange method					
	1	2	3	mean		
Clinker from the Vorovskii factory + 10% $CaSO_4$	4,75	4,71	4,81	4,75	4,84	0,03
Zdolbunovskii cement	3,17	3,22	3,13	3,17	3,25	0,15
Volkhovskii factory cement	1,42	1,47	1,38	1,42	1,47	0,10
Vorovskii factory cement	1,30	1,33	1,27	1,30	1,31	Traces
Bukhtorm construction cement	1,56	1,61	1,52	1,56	1,56	0,13
Kolenerg construction cement	2,25	2,30	2,25	2,27	2,40	0,14
Putsolanov Portland cement	0,87	0.73	0,78	0,78	0,81	0,07
Pikakevskii cement	2,38	2,31	2,28	2,32	2,34	Traces

At the end of the working day the cation exchange resin should also be regenerated with hydrochloric acid, washed two-three times with water, and then, before starting a new determination on the following day, the column should be washed with water until the eluate gives a neutral reaction to methyl orange.

It is best to have 2-3 columns, one of which is being regenerated while the others are being used for the determinations.

It should be pointed out that sulfide sulfur present in cement is not determined when this technique is used. Accordingly, the true gypsum content of the cement is given by the cation exchange method.

The technique developed can be successfully used for controlling the amount of gypsum in many cement factories.

SUMMARY

A method which has been developed for the determination of the gypsum content of cement is based on treatment of the cement with a 5% solution of boric acid, which readily dissolves gypsum and hardly touches the cement base clinker; the solution which is obtained is passed through a column containing a cation-exchange resin in the H-form, and the eluate obtained titrated with sodium hydroxide using methyl orange as indicator.

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QUANTITATIVE DETERMINATION OF ACENAPHTHYLENE

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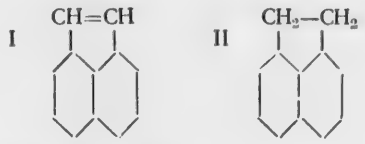
As a consequence of the increased interest in recent years in acenaphthylene (I) as available raw material for the production of plastics, the question of its quantitative determination in the product obtained by the dehydrogenation of acenaphthene (II) has acquired practical importance. Depending on the dehydrogenation condi-



tions, there is a complex mixture of acenaphthylene, unchanged acenaphthene, and large or small amounts of colored and colorless by-products. Quantitative determination of acenaphthylene in such a complicated mixture on the basis of the sparingly soluble acenaphthylene picrate [1,2] is very difficult and is always accompanied by large losses. A photometric method described in the literature by Kynaston and Jones [3] and by Kaufman and Williams [4], for the determination of acenaphthylene was developed using a Spekker absortiometer in conjunction with a mercury lamp. The accuracy of this method is 1%.

For the quantitative determination of acenaphthylene we studied a number of method based both on its unsaturated character and on its intense yellow color. The investigations were carried out on synthetic mixtures of acenaphthylene and acenaphthene. After unsuccessful attempts to determine acenaphthylene by Margoshes' method, we made a careful study of the possibility of determining acenaphthylene by combining it with bromine according to a method described by Isagulyants and Egorova [5]. The method takes into account the halogen used up for the addition reaction as well as for substitution reactions. This is a very important point since the acenaphthylene and acenaphthene present in the test material are readily halogenated. Even this method, however, did not give satisfactory results. When the acenaphthylene content of the test material was high we got low results, while for low contents of acenaphthylene the results were far too high. This is explained by the fact that in addition to incomplete combination of bromine with the double bond of the five-membered ring, there occurs combination of the bromine with the naphthalene nucleus without liberation of hydrogen bromide.

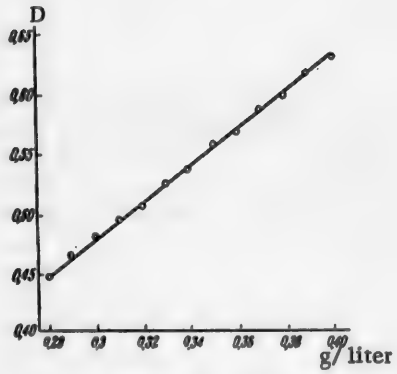
We tried to make use of the capacity of acenaphthylene to polymerize under the action of mineral acids to form a sparingly soluble polymer, hoping in this way to develop a gravimetric method of determining acenaphthylene. The polymerizing agent used was a solution of sulfuric acid in glacial acetic acid. In order to reduce losses during the determination, the latter was carried out in a centrifuge tube, so that it was possible to avoid filtering and transferring the precipitate. A description is given below of a gravimetric method which has been developed as the result of protracted research.

Into a dry tared centrifuge tube is weighed 0.3-0.4 g of test material, which is then dissolved by heating in 1 ml of glacial acetic acid. 1 ml of sulfuric acid (8 g of concentrated sulfuric acid in 20 ml of glacial acetic acid) solution is then added to the hot solution obtained and the whole heated for 15 minutes in a metal block at 125-130° while it is continuously stirred. The contents of the tube are diluted with 5 ml of water and the whole heated to the boil, the precipitate which is formed is ground up for some time with a rod and the contents of the tube finally centrifuged. The clear supernatant liquid is decanted and the polymer which remains is washed

TABLE 1

Gravimetric Determination of Acenaphthylene in Polymeric Form

Acenaphthylene content of the mixture, %	Weight mixture, g	Polymer obtained	Acenaphthylene found, %	Acenaphthylene content of the mixture, %	Weight mixture, g	Polymer obtained	Acenaphthylene found, %
100	0,4120	0,3886	94,32	80	0,4064	0,3463	85,21
100	0,4252	0,4038	94,97	80	0,4118	0,3424	83,15
100	0,4095	0,3884	94,85	70	0,4170	0,3141	75,32
100	0,4118	0,3383	94,29	70	0,4200	0,3176	75,62
90	0,4071	0,3641	89,44	60	0,4130	0,2895	70,10
90	0,4216	0,3831	90,87	60	0,4302	0,2983	69,34
90	0,4032	0,3599	89,26	50	0,4067	0,2298	56,50
90	0,4125	0,3652	88,53	50	0,4114	0,2434	59,16
80	0,4042	0,3410	84,36				



Relation between optical density (D) and acenaphthylene concentration (c).

with 4 ml of alcohol, the tube being heated in the block and the polymer ground up with a rod. After two alcohol washings, the tube plus polymer are placed in a drying oven and dried for 30 minutes at 80°, and then for 60 minutes at 125-130°. Results for the determination of acenaphthylene in synthetic mixtures with acenaphthene are given in Table 1.

Several parallel determinations are given in Table 1 to illustrate the reproducibility of the method. Results of the gravimetric determination of acenaphthylene do not always agree with its actual content in the test mixture, but, thanks to the constancy of the results, which depends on strict observance of the experimental conditions, it is possible to assess the true amount of acenaphthylene on the basis of a calibration curve.

The photometric method is considerably simpler, but it cannot be used directly for the analysis of such a product as that obtained by the dehydrogenation of acenaphthene since this product contains a considerable amount of dark colored, high molecular weight compounds. Vacuum distillation leads to complete removal of the colored compounds which interfere with the determination of acenaphthylene. The speed with which distillation can be carried out, and a high vacuum are of very great importance, in order to avoid resinification and polymerization of the acenaphthylene. Distillation of 20 g of product should not take more than 5-8 minutes, while the residual pressure should not exceed 15 mm. A short-time vacuum distillation is not accompanied by any appreciable resinification of the acenaphthylene. When it is borne in mind that the errors of the methods we have developed for the determination of acenaphthylene lie within the limits of 1%, then it is obvious that the vacuum distillation which precedes determination of the acenaphthylene cannot essentially affect the accuracy of the results.

We have established conditions for the photometric determination of acenaphthylene in the visible part of the spectrum using an ordinary incandescent lamp as the light source. For the visual colorimetric determination of alcoholic solutions of acenaphthylene containing about 0.2 g of this compound in 100 ml of solution, and using a KOL-1 colorimeter with a No. 7 light filter (effective wavelength 449 mμ) the experimental error amounts to 2-3%. For the colorimetric determination of solutions of acenaphthylene containing acenaphthene, it is best to use as a standard reference solution a solution of a mixture of these two compounds containing approximately the same amount of acenaphthylene as the test material. When this is done the experimental error drops and amounts to about 1-2 %.

The best results were obtained when we used the UM-2 universal monochromator with a selenium photoelement. Determinations were carried out at 425 mμ , the thickness of the layer being 20 mm, while the concentration of the acenaphthylene was 0.03-0.04 g in 100 ml of ethanol. In this concentration range the change in optical density of the acenaphthylene solution conforms to Beer's law (see diagram).

As can be seen from Table 2, the experimental error does not exceed 1%.

TABLE 2

Determination of Acenaphthylene in Synthetic Mixtures with Acenaphthene using a UM-2 Monochromator.

Acenaphthylene content of the mixture, %	Acenaphthylene content found, %	Absolute error, %	Acenaphthylene content of the mixture, %	Acenaphthylene content found, %	Absolute error, %
70	69,0	−1,0	87,5	88,2	+0,7
72,5	73,2	+0,2	90	89,7	−0,3
75	75,3	+0,3	92,5	93,6	+1,1
77,5	78,1	+0,6	95	94,8	−0 2
80	79,6	−0,4	97,5	98,0	+0,5
82,5	82,5	0,0	100	99,0	−1,0
85	84,5	−0,5			

SUMMARY

A simple method has been suggested for the isolation of colored and high molecular weight compounds from the crude product obtained by dehydrogenation of acenaphthene. The possibility has been demonstrated of determining acenaphthylene gravimetrically in the form of a sparingly soluble polymer.

A method based on the use of a UM-2 monochromator has been developed for the photometric determination of acenaphthylene in the product obtained by dehydrogenation of acenaphthene.

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* Original Russian pagination. See C.B. Translation.

QUANTITATIVE DETERMINATION OF CYCLOHEXYLNITRITE, CYCLOHEXANONE, AND NITROCYCLOHEXANE IN THEIR MIXTURES

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For the separate determination of cyclohexylnitrite in mixtures, the iodometric method is the form suggested by Beab and Szalkowski [1] for the determination of ethyl- and amylnitrite, was used; the hydroxylamine method [2] was used for the determination of cyclohexanone, while for the determination of nitrocyclohexane a method based on its reduction to the aci-form by means of hydrogen iodide was used [3]. The following original materials were used: cyclohexylnitrite obtained by the action of sodium nitrite on cyclohexanol in an acid medium [4]; commercial cyclohexanol and cyclohexanone; nitrocyclohexane isolated from the appropriate fraction of the nitration products of cyclohexane by dissolving the fraction in 10% NaOH and subsequent precipitation with CO_2. After a two stage distillation, the materials had the following constants: cyclohexylnitrite b.p. 10 mm = 30-32°, $n^{20}D$ 1.4384; cyclohexanone b. p. 760mm = 154-155°, $n^{20}D$ 1.4520; nitrocyclohexane b. p. 40mm = 108-110° $n^{20}D$ = 1.4611; cyclohexanol b. p. 760mm = 160-161°, $n^{20}D$ = 1.4658.

TABLE 1

Compound	Taken, g	Found, %
Cyclohexylnitrite	2,2146	99,7
Ditto	2,5974	99,3
»	2,6155	99,8
Cyclohexylnitrite	0,5485	98,8
Ditto	0,4519	98,6
»	0,4920	97,2
Nitrocyclohexane	1,3106	99,8
Ditto	1,4750	99,5
»	1,0922	99,3

The results given in Table 1 show that the methods chosen give good results for the separate determination of cylohexylnitrite, cyclohexanone, and nitrocyclohexane. It should be borne in mind that the aliquot of cyclohexylnitrite must be dissolved in alcohol immediately prior to determination, since in an alcoholic solution prepared beforehand low boiling ethyl nitrite (+ 17°) is formed as the result of an exchange reaction between alcohol and cyclohexylnitrite, and this can lead to losses when samples are taken.

TABLE 2

Mixture	Composition, g	Found, %
Cyclohexylnitrite	2,1617	99,6
Cyclohexanol	2,6470	—
Cyclohexylnitrite	2,4558	99,8
Cyclohexanone	1,0245	—
Cyclohexylnitrite	0,4033	—
Cyclohexanone	0,5028	118,8
Cyclohexylnitrite	2,0348	99,6
Nitrocyclohexane	1,1472	—
Cyclohexylnitrite	1,3960	—
Nitrocyclohexane	1,4312	105,1
Cyclohexanone	0,5410	98,0
Cyclohexanol	1,7320	—
Cyclohexanone	0,4915	97,8
Nitrocyclohexane	0,5240	—
Cyclohexanone	1,0102	—
Nitrocyclohexane	1,2209	99,7
Nitrocyclohexane	1,3111	99,5
Cyclohexanol	1,1520	—

Cyclohexylnitrite can be determined by the recommended method in the presence of nitrocyclohexane cyclohexanol, and cyclohexanone, but it interferes with the determination of both cyclohexanone and nitrocyclohexane (Table 2). Accordingly, we developed a method for removing cyclohexylnitrite from its mixtures with cyclohexanol and nitrocyclohexane.

Nitrites are known to undergo an exchange reaction with alcohols [5]. Thus, amyl nitrite and propanol react to form propyl nitrite and amyl alcohol. Bearing in mind that methyl nitrite boils at -12°, we made use of the exchange reaction between cyclohexylnitrite and methanol to remove the cyclohexylnitrite:

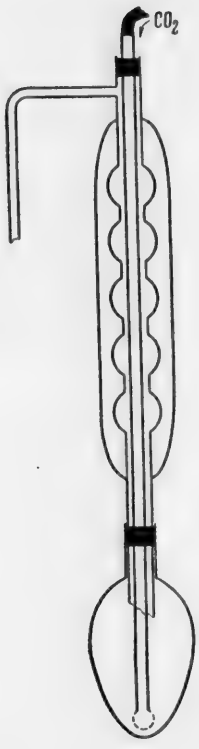
$$C_6H_{11}ONO + CH_3OH \rightarrow C_6H_{11}OH + CH_3ONO$$

TABLE 3

Test mixture					Found, %			
Taken, g	Content, % wt.				Cyclohexylnitrite	After removal of cyclohexylnitrite		
	methanol	cyclohexylnitrite	cyclohexanone	nitrocyclohexane		cyclohexylnitrite	cyclohexanone	nitrocyclohexane
2,6723	—	100	—	—	99,6	—	—	—
2,1261	—	100	—	—	99,6	—	—	—
8,1511*	75,2	24,2	—	—	40,7	—	—	—
7,2260*	75,2	24,2	—	—	35,5	—	—	—
4,4225**	65,2	23,2	11,6	—	—	Traces	97,8	—
5,0273**	65,2	23,2	11,6	—	—	Ditto	98,6	—
10,5911**	55,2	17,6	9,0	18,2	—	»	97,9	99,8
11,2210**	55,2	17,6	9,0	18,2	—	»	97,7	99,7

* The mixture of methanol and cyclohexylnitrite was allowed to stand for 15 minutes uncovered prior to analysis. During this stage a considerable part of the cyclohexylnitrite was converted into methyl nitrite and was removed as CH_3ONO.

** The nitrite was decomposed beforehand and the methyl nitrite formed removed.



The exchange reaction does not proceed to completion with higher boiling alcohols. In order to ensure that the reaction goes to completion with methanol, excess of the latter was taken and the methyl nitrite formed removed from solution by passing CO_2 through it. The technique used for removing cyclohexylnitrite is as follows; methanol (2-3 times the amount of nitrite contained in the mixture) is added to the test solution and the solutions obtained placed in the apparatus shown in the diagram. The apparatus is a flask fitted with a reflux condenser. Through the top of the condenser a tube with a perforated enlargement at the end is introduced into the flask; CO_2 (at room temperature) is passed through this tube. The flow of CO_2 is stopped when the issuing gas gives a negative test for nitrite. The test for nitrite is carried out by attaching a test tube containing acidified KI solution to a side tube fused into the top of the condenser. CO_2 is passed through the apparatus for 10-20 minutes. At the end of this period the contents of the flask are analyzed for their content of cyclohexanone and nitrocyclohexane.

It is clear from the results obtained (Table 3) that cyclohexanone and nitrocyclohexane are quantitatively determined after removal of cyclohexylnitrite.

SUMMARY

It has been shown that cyclohexylnitrite can be quantitatively determined in the presence of nitrocyclohexane, cyclohexanol, and cyclohexanone, but the presence of cyclohexylnitrite interferes with the determination of cyclohexanol and nitrocyclohexane. A method has been developed for removing cyclohexylnitrite. It has been shown that after the cyclohexylnitrite has been decomposed, cyclohexanone and nitrocyclohexane can be quantitatively determined: the ketone by the hydroxylamine method, while the nitro compound is determined by its reduction with hydrogen iodide in the alkaline solution.

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THE DETERMINATION OF HALOGEN IN HALOGEN-CONTAINING COMPOUNDS

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The chief problem during the analysis of organic halogen containing compounds is the conversion of the halogen into the ionic state. A number of techniques have been suggested for this purpose: complete decomposition of the material, e.g. by nitric acid (Carius' method) [1] or by combustion in oxygen with subsequent complete oxidation with hydrogen peroxide or with silver salts; splitting off the halogen by the action of alkali or alkali metals [2]; saponification with alkalis in various aqueous and alcoholic media; the action of metallic sodium in various alcohols and neutral solvents [3]; reduction with nascent hydrogen [4], etc. The conditions used for converting the halogen into the ionic state are chosen in accordance with the structure of the molecules of the test halogen compound. The most general method is Carius' method, the complexity of this method, however, prevents its widespread application. Methods based on the action of alkali, and of alkaline metals in solvents, are used more often.

Ruzhentseva and Kolpakova [5] studied a method which they have suggested on a large number of examples. In the present article we should like to point out several facts observed during the analysis of halogen derivatives, in order to show carefully one must proceed in choosing the experimental conditions.

During the determination of chlorine in aliphatic halogen-containing acids (e.g. 7-chloroheptanoic, 9-chlorononanoic), benzal chloride, and cuminal chloride, using reduction with a skeleton nickel catalyst in an alkali solution, of aqueous ethanol , the results proved unsatisfactory. This was difficult to understand because determination of chlorine in such a material as chlorobenzene by the same method gives good results.

It was thought that an increase in temperature would favor the reduction; accordingly we used alcohols with a higher boiling point than ethanol. Isoamyl- and benzyl alcohols, and ethylene glycol were tried. Since heating in isoamyl and benzyl alcohols was accompanied by strong darkening of the solution we chose ethylene glycol.

On boiling the test halogen compound with a skeleton nickel catalyst in an alkaline solution of aqueous ethylene glycol we got satisfactory results (Table 1).

It might be assumed therefore that in the case of the halogen-containing acids which we tested , dehalogenation on boiling with a skeleton nickel catalyst in an alkaline medium, occurs not as a result of reduction with hydrogen contained in the catalyst [6], but as the result of the action of the alkali.

In order to check on this possibility we carried out a series of test in which the halogen-containing acids were boiled with 0.5 N alkali in 50% aqueous ethylene glycol in the absence of the nickel catalyst. Under these conditions, it was found that the test halogen-containing acids were actually dehalogenated quantitatively. Monochloroacetic acid which was analyzed by the authors of the work cited by means of a skeleton nickel catalyst, was quantitatively dehalogenated on boiling with 0.5 N alcoholic potassium hydroxide.

Satisfactory results were also obtained during the determination of chlorine in other materials (Table 2).

Reduction by means of hydrogen is not always superfluous . For example, chlorine in chlorobenzene can be determined with reasonable accuracy only by the method of Ruzhentseva and Kolpakova, or by the Stepanov method which is arbitrarily based on a reduction reaction.

TABLE 1

Acid	Weight taken, g	0.1 N $AgNO_3$ used for titration, ml	Amount of Cl, %		
			calculated	found	found by combustion
5-Chloroheptanoic	0,1430	10,14	26,0	25,3	26,0
9-Chlorononanoic	0,1136	5,85	18,40	19,27	18,21
11-Chlorounde-canoic	0,1072	4,87	16,10	16,10	16,3

TABLE 2

Compound	Weight taken, g	0.1 N $AgNO_3$ titer, ml	Amount of Cl, %		
			calculated	found	found by combustion
5-Chloropentanoic acid	0,1390	10,1	26,0	25,8	26,0
7-Chloroheptanoic acid	0.2437	15,0	21,6	21,8	21,9
9-Chlorononanoic acid	0,1627	8,4	18,4	18,3	18,21
11-Chloroundecanoic acid	0,1545	7,04	16,2	16,17	16,3
Benzal chloride	0,0374	4,65	44,09	44,12	44,1
Cuminal chloride	0,0227	2,21	34,9	34,6	34,59
Chloroacetic acid	0,0849	8,52	37,5	35,73	35,86

In the case of halogen determination in halogen acids with an open chain of carbon atoms, it is probably true to say that the reaction is simply one of saponification with alkali which depends on the temperature. There is no simple, universal method, for the determination of halogen-containing compounds.

Chlorine is determined by adding to 0.1 g of test material 4 g of a paste of skeleton nickel catalyst, 25 ml of 0.5 N KOH in ethylene glycol and 15 ml of 10% aqueous NaOH solution. The mixture is boiled under reflux for half an hour on a sand bath. On completion of the reaction the condenser is washed with water, the catalyst filtered and then washed with distilled water until the wash liquors give a negative test for chloride ions (test with $AgNO_3$). The filtrate is acidified with nitric acid and a Volhard titration carried out. A blank is carried out at the same time.

For determination of chlorine in halogen-substituted acids, benzal- and cuminal chloride where no catalyst is needed, the following procedure is adopted: about 0.1 g of test material is placed in a 100-150 ml reaction flask and 20 ml of 1 N NaOH in 50% aqueous ethylene glycol pipetted into the flask. The reaction mixture is heated on a sand bath for 1.5 hours. When the reaction is complete the mixture is neutralized and acidified with nitric acid, and the chlorine determined by a Volhard titration. The results obtained are shown in Table 2.

SUMMARY

Reduction by a skeleton nickel catalyst in an aqueous alcohol medium does not give quantitative results for the determination of chlorine in aliphatic halogen-substituted acids.

It has been shown that in these cases quantitative results can be obtained by using 0.5 N alkali in a high-boiling solvent. The most suitable solvent found was 50% aqueous ethylene glycol.

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MIRRA OSIPOVNA KORSHUN

(1900-1958)

Soviet analytical chemistry has suffered a serious loss: on December 1, 1958 after a serious illness there occurred the death of Mirra Osipovna Korshun a member of the Analytical Commission of the Presidium of the USSR Academy of Sciences, a member of the Commission on Microchemical Methods of the International Union of Pure and Applied Chemistry, and the director of the Laboratory of Microanalysis of the Institute of Hetero-organic Compounds of the USSR Academy of Sciences. M. O. Korshun was a pioneer of organic microanalysis in the Soviet Union. She devoted all her working life to the development of this important branch of chemistry.

Mirra Osipovna Korshun was born on August 21, 1900 in Wilno. She started her working life at an early age as a pharmaceutical student apprentice; her thirst for knowledge led her to undertake hard work in pharmacies and chemical factories. In 1929 she finished her course in the chemical faculty of Moscow State University in the organic chemistry section. At first she worked as a chemist in an industrial laboratory and was appointed leader of the analytical group in 1933. Her work in the field of elemental microanalysis dates from this period.

In 1937 she organized and became head of the laboratory of microanalysis, first in the Institute of Organic Chemistry, then, from 1954, in the Institute of Heteroorganic Compounds of the USSR Academy of Sciences; here she continued as director till her death.

M. O. Korshun became an active propagandist for micromethods of elemental analysis—a field of analytical chemistry which was almost undeveloped at that time in the Soviet Union. Alive to all questions of organic synthesis, M. O. Korshun came to adopt the classical methods of microanalysis. Thanks to her great scientific intuition, her profound knowledge of analytical chemistry, and thanks to her experience coupled with her unusual industriousness M. O. Korshun found her calling in organic analysis. A new, original principle for the rapid pyrolytic combustion of organic materials, in an empty tube in a rapid stream of oxygen, which she has suggested, has proved very fruitful. The wide application of this principle based on an all-round study of the mechanism of pyrolytic combustion, led M. O. Korshun to develop a whole series of so called "rapid methods of microelemental analysis". Using these methods it has proved possible to determine simultaneously three to four elements on one aliquot of material amounting to a few milligrams; thus, it is possible to carry out a simultaneous determination with carbon and hydrogen of such elements as sulfur or halogen; phosphorus, sulfur or halogen; silicon; metal and

halogen; metal and sulfur. The principle of preliminary pyrolysis led M. O. Korshun to develop a method for the direct determination of oxygen together with halogen, and also methods for the determination of sulfur and nitrogen by hydrogenation, and nitrogen in a carbon dioxide stream. Rapid methods of analysis include methods for the simultaneous determination of halogens in organic materials after decomposition of the latter with metallic potassium in a bomb; these methods have also been developed by Korshun.

The results of M. O. Korshun's studies have been published in her monograph "New Methods of Elemental Microanalysis", which has already been published in China, and is going to be published in America and England. She has left behind her about 50 scientific papers. Her death interrupted her work on a second, enlarged issue of her monograph.

The success of the new methods and their rapid adoption had a lot to do with the active participation of M. O. Korshun in preparing cadres of qualified microanalysts, in creating a Soviet school of microanalysis and organizing a number of large laboratories (in factory No 51, in the Institute of Organic Chemistry in the Institute of Heteroorganic Compounds of the USSR Academy of Sciences, in the old and new buildings of Moscow State University), and also in guiding standardization, and in introducing microanalytical apparatus and weights into industrial production.

M. O. Korshun's activity was rewarded by the Soviet Government by the award of the Order of the Red Banner of Labor, and by the Badge of Honor and other medals.

In M. O. Korshun we have lost not only a first-rate scientist, and an outstanding organizer, but also a person, liberally endowed with such qualities as a highly developed sense of civic duty and an honest attitude toward work. All these qualitites were combined in M. O. Korshun together with modesty and personal charm. The memory of M. O. Korshun as a fine, cordial person, untiringly serving science in our country will always remain with those who knew her.

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